FRONTISPIECE.

Photo, S. E. Jacobson. *Trinidad.*

CACAO PODS.

COCOA AND CHOCOLATE

THEIR CHEMISTRY AND MANUFACTURE

BY

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PREFACE

IT has been the object of the author in producing this work to provide a standard book of reference dealing with cacao from its growth till manufactured into cocoa or chocolate.

For the first time the chemical composition of cacao has been traced from the fresh beans through the various stages of manufacture, so that the changes which occur during fermentation, drying, roasting, etc., may be followed.

The most recent methods of analysis have been discussed, and the author has only recommended those which he himself has found to give accurate and consistent results.

Throughout the book the word *cacao* has been used for the raw material, that is to say, for the beans or their parts from which nothing has been taken or which have had nothing added to them; for example, after roasting and husking the *cacao* beans, the *cacao* nibs are expressed and the fat is removed with the formation of *cocoa* powder. The word *cacao* is also used before "butter," signifying the fat extracted from the *cacao* bean, owing to the possibility of confusion with coconut fat (obtained from *Cocos nucifera*).

I am glad of this opportunity to thank those who have assisted me in this work, and especially Mr. G. H. Davis and Mr. W. P. Paddison. My thanks are also due to Messrs. Baker & Sons, Ltd., of Willesden, and Messrs. Bramigk & Co., for their permission to reproduce photographs of their most up-to-date machinery.

R. W.

DITTON HILL,
SURREY.

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INTRODUCTION

"The persons who habitually take chocolate are those who enjoy the most equable and constant health and are least liable to a multitude of illnesses which spoil the enjoyment of life." In such words does Brillat Savarin* describe the virtues of chocolate, and whether from the fact that cacao preparations do actually assist in maintaining good health, or for the reason that chocolate is the most pleasing confection to the palate, it is certain that the growth of the cacao industry in the last three centuries is little short of remarkable.

First as a beverage, then as a sweetmeat, chocolate has steadily worked its way into public favour, and it is safe to say that in no civilised country of the world is the "Prince of Sweetmeats" unknown, and that wherever civilised man has explored, travelled or sojourned, there may be found a wrapper, yellow, blue, red or white, that once contained a tablet of some well-known brand.

The popularity of chocolate is well deserved, for, besides being a sweetmeat, it possesses a food value of a high order.

Dr. Johnson has shown that cocoa essence contains as much flesh-forming bodies as the solids of dried milk, and Professor Forster† has compared the heat-giving power of

* Brillat Savarin, 'Physiologie du Goût.'

† Prof. J. Forster, 'Ueber Holländische Kakao. Ein Beitrag zum Verständniss der Bedeutung des Kakaos als Genuss- und Nahrungs-Mittel.'

cacao and its preparations with some of our most valuable foodstuffs. Thus:

1 kilo of lean beef	gives 1,214	calories.
1 ,, fat beef	,, 3,057	,,
1 litre of cow's milk . . .	,, 672	,,
1 kilo of hens' eggs (av. 18 eggs) .	,, 1,678	,,
1 ,, husked earth nuts . .	,, 5,184	,,
1 ,, peas	,, 2,710	,,
1 ,, white bread . . .	,, 2,528	,,
1 ,, cacao beans . . .	,, 5,110	,,
1 ,, cacao mass . . .	,, 5,967	,,
1 ,, cacao powder . . .	,, 4,167	,,
1 ,, chocolate	,, 4,763	,,

These figures, which show the true food value of various of our nourishing foods, explain the remarkable sustaining power of cacao preparations, a characteristic which is recognised at the present time by our explorers, athletes, soldiers, sailors and others engaged in work or pastimes which entail great physical endurance.

The ancient Mexicans also appreciated the stimulating and sustaining properties of chocolate, for Benzoni tells us that during the time of festivities "they used to spend all the day and half the night in dancing with only cacao for nourishment."

Apart from the valuable properties of chocolate as a food, there lies the all-important fact that it is pleasing to the palate. All classes, all ages, all sexes, at all times and in all places now eat chocolate because they like it and not because it is a stimulating and nourishing food, and it is this class of consumer that appeals to the

manufacturer, and which enables him to produce a good, wholesome and palatable preparation within the reach of all.

Did time and space allow, there is much to be told on the romantic side of chocolate, of its divine origin, of the bloody wars and brave exploits of the Spaniards who conquered Mexico and were the first to introduce cacao into Europe, tales almost too thrilling to be believed,* of the intrigues of the Court of Spain, and of celebrities who met and sipped their chocolate in the parlours of the coffee and chocolate houses so fashionable in the seventeenth and eighteenth centuries.

But there is little room for romance in a technical work of this sort, or in these prosaic days, when even the "Odour of Sanctity" has been reduced to a chemical formula. The "Food of the Gods" is now nothing but a scientific blending of certain chemical compounds, and chemists, instead of priests, are protecting the fair name of chocolate.

* Prescott's 'Conquest of Mexico,' and Ogilby's 'Description of America,' etc.

PART I

HISTORY, BOTANY, AND AGRICULTURE OF CACAO

CHAPTER I

HISTORY AND GROWTH OF THE CACAO INDUSTRY

The commercial history of cocoa and chocolate commences with the introduction of the cacao bean into Europe in the year 1528, when Cortes, the conqueror of Mexico, returned to the court of Spain, bringing with him a large collection of minerals, animals, and plants to show the resources of the newly acquired country.*

Previous to this, however, the beans of the cacao tree were much used by the Aztecs, the Aborigines of Central America, who not only prepared from them the beverage known as "chocolatl," but also made use of them as a means of currency, described by Peter Martyr as "blessed money, which exempts its possessors from avarice, since it cannot be long hoarded, nor hidden underground."†

The royal revenues of Mexico were raised by imposing a tax on all the agricultural produce and manufactures of the kingdom, and among the items of the tribute furnished by different cities Mendozza quotes—20 chests of chocolate, 40 pieces of armour, a chest of maize, 8000 lumps of unrefined copal, 100 copper axes, 80 loads of red chocolate, 800 "xicaras"—vessels out of which they drank chocolate, 4000 loads of lime, 40 bags of cochineal, 20 bags of gold-dust, 200 loads of chocolate, 8000 "handsful" of rich scarlet feathers, etc.

* Prescott, 'Conquest of Mexico.'

† 'De Orbe Novo,' dec. v, cap. 4.

Torquemada has extracted the particulars of the yearly expenditure of the Mexican palace from the royal account book, which included 2,744,000 fanegas of cacao, an amount approximately equal to 100,000 tons, besides 8,000 turkeys, a quantity of maize about equal to 200,000 tons, and an incredible amount of game, vegetables, and condiments of every kind.

The value of the cacao beans as coins depended upon their size, and may have been primarily looked upon as valuable from the mythical history of their origin.

The history of cacao as given in Mexican mythology is not without interest, for it would appear from one of the most sacred traditions of the Indians of Mexico that we are indebted to Divine providence for its introduction to earth. Quetzalcoatl, god of the air, was commissioned to convey to man the seeds of the "quacahault" or cacao tree, which was one of the few growing in Eden for the delectation and food of the gods and the first sons of the Sun.

In the golden days of Anahuac or Mexico, when the "garden prophet" resided on earth, the land teemed with fruits and flowers without the pains of culture; a single ear of Indian corn was as much as a man could carry, and the cotton, as it grew, was dyed to the hues required by man. The air was filled with intoxicating perfumes and the sweet melody of birds, and things were always as they ought to be.

Quetzalcoatl incurred the wrath of one of the principal gods and was compelled to abandon the country, but he was so much beloved by the people of Mexico, to whom he had taught the use of metals, agriculture and the arts of government, that his return was looked for with confidence and pleasure, and a temple and altar were erected to his worship. He was said to have been tall of stature, with a white skin, long dark hair and a flowing beard, and this

description, corresponding in the main with that of Cortes at the head of the Spanish invasion, prepared largely for the easy acceptance of the Spaniards into the hearts of the people. The "garden prophet" was worshipped under the name of Votan, which signified "an adder clothed with precious or divine feathers," a highly complimentary title; and besides the usual offering of burnt incense, his worshippers were wont to lacerate their tongues, as further proof of their devotion—a proceeding which, in these days, would hardly be considered complimentary, as it might imply that they were not desirous of tasting the "food of the Gods."

The emperor Montezuma took no other beverage than chocolate, flavoured with vanilla or spices, and so prepared as to be reduced to "a froth of the consistency of honey."

Golden goblets, with spoons of the same metal, or of tortoiseshell finely wrought, were used by Montezuma for drinking his chocolate, and the cup, after being drained, was thrown into the lake surrounding the palace.

At the conquest of Mexico a vast quantity of treasure was taken from the lake, and judging from the number of goblets found, and the amount of chocolate prepared daily for the emperor's consumption ("50 jars or pitchers"), it may be assumed that Montezuma was not altogether averse to the beverage.

The beans were roasted in earthenware vessels, ground between stones, and mixed with cold water, to which was sometimes added a dash of capsicum, probably as a flavouring material, though possibly as a means of increasing the devotion of the sore-tongued worshippers of Votan.

The richer people flavoured their chocolate with vanilla or spices, and sweetened it with sugar or honey. The liquid was whipped into a froth, and one early historian is careful to point out the importance "of opening the mouth wide, in order to facilitate deglutition, that the foam may dissolve gradually and descend imperceptibly as it were,

into the stomach," and closes with a eulogy on the beverage so prepared.

The exact date of the introduction of cacao into Mexico from Eden is obviously rather difficult to determine, but De Candolle,* who has made a close study of the history of all plants of economic importance, states with some assertion that the tree has been in cultivation in America for three or four thousand years.

The planting of the seed seems to have called for special ceremony among the original cultivators, the shedding of the blood of man, beast or fowl being apparently one of the necessary operations.

Bancroft, writing of the Maya races of the Pacific, says: "Before planting the seed, they hold a festival in honour of their gods, Ekchuah, Chac, and Hobnil, who were their patron deities. To solemnise it they all went to the plantation of one of their number, where they sacrificed a dog having a spot on his skin the colour of cacao. They burned incense to their idols, after which they gave to each of the officials a branch of the cacao plant."

According to Ximinez, the blood of slain fowls was sprinkled over the land to be sown, a performance certainly more profitable to the soil than mere sacrifice.

History does not relate of the cacao tree being of any commercial importance, however, until the conquest of Mexico, when the Spaniards found the people of the country fully appreciative of its value.

For some years the Spaniards kept the secret of chocolate preparation in their own hands, so closely that we read that during the war between Holland and Spain, the Dutch sailors, on finding cacao beans in some Spanish ships which they had captured, threw them overboard with the scornful description, "*Crottes de brebis*."

The Spaniards did not long remain in undivided

* 'Origin of Cultivated Plants'

possession of their secret, for in 1606 we find that one Antonio Carletti, who had himself learnt to appreciate the fine qualities of the beverage in Spain, was instrumental in bringing them to the notice of the Italians.

From this time onwards the popularity of cacao preparations spread freely to all parts of Europe, though in 1624 Franciscus Rausch, in a book which had a wide circulation and was published in Vienna, stated that the consumption of chocolate was largely responsible for the committal of many excesses, especially in the case of monks, for whom he urged that its use should be forbidden.

This, however, was an isolated case of attack against the use of chocolate, and the latter part of the seventeenth century was particularly prolific with its crop of articles and treatises lauding chocolate as a pleasing and nourishing beverage.

The idea that chocolate inflamed the passions was prevalent for a long time, however, and even as recently as 1712 the 'Spectator' states, "I shall also advise my fair readers to be in a particular manner careful how they meddle with romances, chocolate, novels and the like inflamers, which I look upon as very dangerous to be made use of during this great carnival" (the month of May).

Chocolate made its first appearance in France in the reign of Louis XIII, probably through the agency of Carletti, who was teaching all Europe the process of roasting the beans, in spite of the fact that the Spaniards were still jealously attempting to guard the method of preparation.

In 1659, one Challon David obtained the monopoly in France for making and selling chocolate, a privilege which was renewed in 1666 for twenty-six years. His factory is said to have been near to the Croix du Tiroir at the corner of Rue de l'Arbre-Sec and the Rue Saint Honore.

Under Louis XIV the use of chocolate became very

general in the country, and the advent of the first crop of cacao grown in the French colony of Martinique in 1679 marked the first step of organised cultivation.

In 1692 the monopoly of chocolate manufacture and selling, which had been previously in the hands of David, was transferred to Damame, who was entitled to hold it for six years.

One year later, however, in 1693, we find the privilege was extended to all confectioners and grocers, Louis XIV apparently seeing in the new industry a means of increasing his private revenue.

At this time there were only very small quantities of cacao in the hands of private individuals, as the high price of the beans, which were only obtained through Spain from Central America, was a serious hindrance to the general use of chocolate, and it is interesting to note, when we come later to discuss the world's output of cacao at the present time, that the man Rodolphe de Canvillet, whose name should be handed down to posterity as declaring to the revenue officers the greatest amount of cacao in any individual's possession, was the owner of exactly 10 lb., and that the total amount of beans declared in France did not exceed 22 lb.

In about 1680 the Spaniards had carried cacao from Acapulco to the Philippine Islands, where we are told by Blanco ('Fl. de Filipinas,' edit. 2, p. 420) it thrived exceedingly, though no record of the arrival of the first Philippine crop is recorded.

The use of chocolate seems to have been known both in England and Germany in the middle of the seventeenth century, when coffee and chocolate houses were in high vogue in both countries. "White's," of the Haymarket, celebrated for its chocolate and fashionable customers alike at the commencement of the eighteenth century, was typical of the many which existed at this time.

Our earliest botanical historians show some divergence of opinion as to the native land of Cacao. Humboldt * states that the cacao tree "grows wild in the forests of the Amazon and Orinoco basins"; Schach † says that it is also to be found in the wild state in Trinidad; and De Candolle, the greatest authority, doubts whether the cacao plant is indigenous to Guiana, and continues, "Many early writers indicate that it was both wild and cultivated at the time of the discovery of America, from Panama to Campeachy; but from the numerous quotations collected by Sloane ‡ it is to be feared that its wild character was not sufficiently verified."

Cacao was said to have been cultivated in Jamaica in the early part of the seventeenth century, but according to Long in his 'History of Jamaica,' the plantations were destroyed by a "blast."

It must have been about the same time that disaster overtook the plantations of Trinidad, for Sir A. de Verteuil mentions in his work on Trinidad that, "In the year 1727 a terrible epidemic spread in the cacao plantation," a catastrophe which resulted in complete ruin.

Some thirty years later the cacao industry was revived in the islands by the Capuchin Fathers, who introduced the hardier but inferior Forastero cacao, which Sir A. de Verteuil tells us is the variety at present cultivated on the island of Trinidad.

Previous to the importation of the Martinique crop into France in 1679, there is little doubt that all the cacao consumed was obtained from Central America, as there is no real evidence to show that the cacao tree was known to be growing wild or in cultivation elsewhere.

The results of such a limited area of supply very

* Humboldt, voy. ii, 511.

† Grisebach in 'Flora of Brit. West Indies,' 91.

‡ Sloane, 'Jamaica,' ii, 15.

naturally caused earlier cacao preparations to assume a high price, and was for a long time a serious hindrance to their general use among all classes. The improvements of means of transport and the enterprise of planters and manufacturers have now enabled chocolate in all forms to be placed within the reach of even the very poor, a condition of affairs which has greatly popularised chocolate confections, evidenced by the ever-increasing demand.

The first record of the manufacture of chocolate on the large scale is about 1756, when it is said Prince Wilhelm von der Lippe erected a factory at Steinhude, and brought over Portuguese especially experienced in the art of chocolate preparation.

France claims to have been the first to erect a factory with mechanical devices for the preparation of chocolate, the honour being due to M. Carbone, who seems to have been inspired by the possibilities of driving the machinery by water power in the same way as his oil mill, which he conducted in conjunction with his chocolate factory.

In those days the world's output of cacao was extremely small, and it is interesting to note that in 1909 it was estimated that a total of 391 million pounds of cacao was put upon the market, and that many hundreds of factories were busily at work in all countries, presenting cocoas and plain and fancy chocolates to an ever-ready public.

The increasing supply of, and demand for, cocoa and chocolate is clearly exemplified in the growing imports of the raw materials.

England, France, Germany, United States, Holland, Switzerland and Russia, all show largely increasing imports of cacao beans, the figures for home consumption in each country showing a similarly large increase.

H. Jumelle* estimated the consumption of cacao in

* Jumelle, 'Le Cacaoyer,' 1900.

Europe in 1900 as close upon 65 million kilos. Of this quantity*—

Germany	consumed	20	million	kilos.
France	,,	16	,,	,,
England	,,	12	,,	,,
Spain	,,	10	,,	,,
Russia	,,	1	,,	,,

This estimation of cacao consumption in England, approximately equal to 26½ million pounds, seems too low when the 1900 official return of raw and manufactured cacao consumption for the United Kingdom is compared with it.

The following table shows the official return of the consumption of coffee and cacao for the United Kingdom for the ten years 1899–1908:

TABLE I.

	Coffee (cwts.)	Cacao (lbs.) (Raw and manufactured).
1899	259,949	39,372,972
1900	260,425	44,569,740
1901	283,606	49,882,354
1902	255,567	53,688,597
1903	268,820	51,042,005
1904	257,540	55,286,457
1905	257,612	54,872,920
1906	255,679	52,617,249
1907	261,096	55,023,420
1908	260,675	56,566,515

From these figures it will be seen that while the consumption of the coffee has remained practically stationary over these years, cacao shows a very steady and pronounced increase.

* The United States, which is not included in Jumelle's estimate, was at the head of all cacoa consuming countries for the year ending June 30th, 1909, a total of 130 million pounds of cacao, raw and manufactured, being recorded for that country.

This increase in favour of cacao over coffee is noticeable in the imports of other countries, notably of Germany, for according to statements published by the Association of German Chocolate Makers* the consumption of coffee increased in that country 24 per cent. between 1886 and 1898, while cacao increased 330 per cent. over the same period.

The imports of coffee and cacao for the two extreme years were as follows :

	Coffee.	Cacao.
1886	1,236,305 quintals†	36,867 quintals
	(approx. $2\frac{1}{2}$ million cwts.)	(approx. 8 million lbs.)
1898	1,532,704 quintals	154,649 quintals
	(approx. 3 million cwts.)	(approx 34 million lbs.)

Although a very large quantity of cacao goes direct from the planter to the factory, a considerable amount finds its way into different American and European markets.

The most important of the latter with the varieties dealt with are here appended :

London.—Guayaquil, Trinidad, Grenada, Carupano, Surinam, Caracas, and Bahia.

Hamburg.—Guayaquil, Caracas, Carupano, Puerto Cabello, St. Domingo, San Thomé, and Cameroon.

Havre.—Maragnan, Haiti, Caracas, Guadeloupe, Martinique, Trinidad, and Ecuador.

Liverpool.—Guayaquil, Bahia, and St. Domingo.

Bordeaux.—Guayaquil, Caracas, and Carupano.

Marseilles.—Brazil, Martinique, Guadeloupe, and Venezuela.

Lisbon.—San Thomé.

Santander.—Guayaquil, Caracas, and St. Domingo.

Amsterdam.—Surinam and Java.

* 'Verband. Deutsch. Schokoladefab.,' xix. No. 7.

† 1 quintal = 1·9684 cwt.

Antwerp.—St. Domingo and Bahia.

Holland, which is a very large consumer of cacao, obtains it chiefly from Antilles, Brazil, Columbia, Ecuador, Venezuela, and the Dutch East Indies, and from the markets of Belgium, France, Great Britain, Hamburg, Portugal, and Prussia.

Of the total quantity imported into Holland, only a relatively small amount is again publicly sold, the figures for the years 1900 to 1904 inclusive being:

	1900.	1901.	1902.	1903.	1904.
Java (bales of 50 kilos)	18,661	19,938	13,144	15,059	19,390
Surinam (bales of 80–100 kilos)	744	635	617	494	372
Caracas and Puerto Cabello	210	242	—	—	197
Haiti, San Thomé, Trinidad, Ceylon, etc.	—	—	—	—	925

The trade done in cacao and its preparation by Holland for the years 1902 and 1903 is strikingly shown by the following figures:

	1902.	1903.
Import of cacao	14,666,274 kilos	16,741,665 kilos.
,, ,, chocolate (without sugar)	97,349 ,,	48,227 ,,
,, ,, ,, (with sugar)	61,186 ,,	94,660 ,,
Export of cacao	5,943,970 ,,	6,011,192 ,,
,, ,, chocolate (without sugar)	3,873,329 ,,	4,962,340 ,,
,, ,, ,, (with sugar)	651,802 ,,	572,354 ,,

CHAPTER II

BOTANY AND NOMENCLATURE

Linnæus, in his classical work of 1720, gave to the cacao tree the dignified name of "*Theobroma cacao*," signifying cacao as "Food of the Gods."* In so doing he was either actuated by a desire to give to the origin of his favourite beverage an honourable and distinguished title, or else he was influenced by a treatise published in 1684 by Buchat, a French doctor, who described chocolate as an invention more worthy of being called food of the gods than nectar and ambrosia.

It is probable, also, that the Mexican word for chocolate, "chocolatl" (supposed to be derived from "choco," "cacava," or "cacana," = the fruit of the tree "quacahault," and "latl" = water), supplied him with the species designation.

Theobroma cacao is the one of the several species native to the tropical regions extending from Mexico to Brazil, which supplies the greater quantity of cacao beans for cocoa- and chocolate-making purposes, and which is chiefly cultivated for its good quality and yield.

Among the most important species of the genus *Theobroma* are *T. bicolor*, *pentagona*, *sylvestris*, *ovatifolia*, and *augustifolia*, all said to be quite distinct from *Theobroma cacao*.

Theobroma bicolor, or "tiger cacao," has been used in

* Greek Θεος = God; βρωμα = food.

Nicaragua for confectionary purposes, but apparently pure eating chocolate has not been made from the beans.

The pods are hard and woody, and show ten ribs, of which every alternate one is considerably more pronounced than its neighbours. The beans obtained from this variety are medium in size and when cut are quite white in colour.

J. Jones,* Curator of the Botanic Gardens, Dominica, submitted bulk samples of the beans to Messrs. J. S. Fry & Sons, Ltd., Rowntree & Co., and Cadbury Bros., to be made into chocolate, and from the reports returned by these manufacturers it would appear that this variety is entirely unsuited for chocolate making and of practically no commercial value.

On the other hand, the beans of *Theobroma pentagona*, or "alligator cacao," received most favourable reports from two of these chocolate manufacturers, whilst the third doubted whether the peculiar taste, different from the usual variety, would meet with approval from the English public.

T. pentagona was brought to Trinidad by Hart in 1893 from Nicaragua, and the shoots were grafted to Forastero stock then in cultivation in the island. The pods possess five district ribs, and are thin-shelled. The beans are large, and when cut across are mostly white, and were thought to be of excellent quality and to contain a higher percentage of fat than *T. cacao*. When roasted, Messrs. Cadbury Bros. report the beans to be "bold and of good colour," but not suitable for making drinking cocoa owing to lack of strength.

The variety of names given to *Theobroma cacao* growing in different climates and soils must not be considered as constituting different "species," but rather "varieties," arising from seed selection, cross-breeding, and natural causes.

* J. Jones, 'W. I. Bulletin,' 1910, x, 337.

The botanical description of the genus *Theobroma*, as given in Grisebach's 'Flora of the British W. Indies,' is as follows:

"Calyx 5 partite, coloured. Petals 5; limb cucullate, with a terminal; spathulate appendage. Column 10 fid, fertile lobes, bi-antheriferous; anthers bilocular. Style 5 fid. Fruit saccate, 5-celled; cells pulpy, polyspermous. Embryo ex-albuminous; cotyledons fleshy, corrugate. Trees; leaves entire; pedicals fascicled or solitary, lateral."

The cultivated tree, *Theobroma cacao*, grows to a height of 25 ft., though it has been met with as high as 40 ft. In Trinidad the tree averages about 15 to 20 feet in height, the lateral diameter of the branches being about the same measurement.*

The flowers of the cacao tree are very small, and in a manner similar to those of many other tropical trees, are carried on the main stem of the branches and on the trunk, singly or in clusters.

The blossoms, though of a bright red hue, are quite insignificant, and in due season are succeeded by pods of an angular cucumber shape, at first green, but becoming yellow and red on ripening.

The period elapsing between "setting" and "ripening" is about four months.

The fruit pods hanging away from the leaves and in singularly isolated positions on the main and strongest parts of the tree present a curious spectacle to agriculturists of temperate climes, though in the tropics it is not an uncommon sight among trees bearing heavy fruit (Pl. I).

It is probable that such an arrangement of flower and fruit has been produced from the necessity of placing small flowers in prominent positions for their better detection and fertilisation by insects, and of providing strong sup-

* J. H. Hart, 'Cacao.'

PLATE I.

Photo, S. E. Jacobson.] *Trinidad.*

THEOBROMA CACAO. (See p. 16.)

ports on which heavy fruit could ripen and produce seed for the perpetuation of its kind.

The trees produce leaves, flowers, and fruit throughout every month, and in the West Indies the crop is gathered twice in the year, the first time in May or June, the second in November or December.

The fruit when ripe is of a rich golden-red colour. Within an outer shell, of about half an inch thickness, is contained a sweetish pulp, enclosing twenty to forty almond-shaped seeds, which, when fermented, finished and dried, represent the cacao beans of commerce.

Opinion is considerably divided as to how the varieties of cultivated cacao should be classified, and though in the main all systems are based upon the appearance of the beans, there are certain botanical differences which enable a closer system of classification to be established.

J. H. Hart, in his treatise on 'Cacao,' makes the following divisions of the varieties cultivated in Trinidad :

Class I : Criollo—fine ; thin skinned.

(1) Variety (*a*) *amarillo* (yellow).
(2) ,, (*b*) *colorado* (red).

Class II : Forastero—thick-skinned.

(3) Variety (*a*) *Cundeamor verugosa amarillo.*
(4) ,, (*b*) ,, ,, *colorado.*
(5) ,, (*c*) ordinary *amarillo.*
(6) ,, (*d*) ,, *colorado.*
(7) ,, (*e*) *Amelonado amarillo.*
(8) ,, (*f*) ,, *colorado.*

Class III : Calabacillo—small podded ; thick, smooth-skinned ; flat-beaned.

(9) Variety (*a*) *amarillo.*
(10) ,, (*b*) *colorado.*

Though other systems of classification divide the varieties into more or fewer classes, amongst the latter

being Sir Daniel Morris's * method of including Calabacillo under Forastero, all existing cultivated cacaos can be included under one of the three headings given by Hart.

Criollo cacao trees are not so sturdy and do not produce such regular crops as those of the two latter classes. The shells of the pods are soft and relatively thin. The bean fresh from a Criollo pod, of either red or yellow variety, is quite rounded, and when cut shows a white, or nearly white, interior, which is not so bitter or harsh to the palate as that of the Forastero, which in turn is less harsh than Calabacillo varieties. The shells of beans also of Criollo cacao are thinner than those of either of the other varieties.

From Criollo cacaos are obtained the finest beans for chocolate and cocoa making, those of Java and Ceylon being typical of this class.

Caracas or Mainland cacao is usually placed in the Criollo class, though some of the lower quality Caracas is undoubtedly of Forastero origin.

Forastero, which include the finest Venezuelan and certain strains of Caracas cacaos, are distinguished by the pale purple interior of their beans when cut fresh from the pod. The shell of the pod is relatively hard and thick, and bears deeper and more pronounced channels running the length of the pod than either Criollo or Calabacillo, thus making the cross-section of the pod star-shaped.

Calabacillo cacaos, which Sir Daniel Morris, the Commissioner of Agriculture for the West Indies, includes under the class heading of Forastero, are formed into a separate division by Hart.

The tree of this variety is the strongest grower and hardiest of all, and is chosen by planters for growing on very poor soil and under climatic conditions unsuitable for

* D. Morris, 'Cacao: How to Grow and How to Cure it.'

the finer and more delicate cacaos. The pods of Calabacillo are small, smooth, and very much more rounded than those of either Criollo or Forastero cacaos. The beans are flat and have a bitter and astringent taste—characteristics which are typical of beans of inferior quality and low market value.

CHAPTER III

THE AGRICULTURE OF CACAO

A. Selection of Site, Soil, Manure, Seed

The cacao planter, in common with his brethren, the fruit farmer and the agriculturist of every clime, must be a man of considerable observation and determination, for the successful culture of his crop is largely dependent upon an intimate knowledge of the natural conditions existing in the place selected for his plantation and upon the pluck with which he faces the possible destruction of his trees by disease or by the "act of God," more to be feared in tropical than in temperate regions.

Science, which of recent years has been directed more and more to agriculture, has proved a useful asset to the cacao planter, helping both his "observation" by giving reasons for observed phenomena, and his "determination" by putting into his hands weapons with which to combat disease.

In these days of severe competition it is most necessary that the planter should possess modern scientific knowledge of soil value and such other items of agricultural chemistry as concern the improvement in quantity and quality of his crop.

In this and the following chapter, though it is impossible to deal fully with these questions of much economic importance to the cultivator, chocolate maker and public alike, an attempt has been made to show how the quality and yield

of cacao beans may be influenced by the natural condition of soil, climate, and kind, by the application of scientific methods to the culture of the cacao tree, and by the processes rendering the beans fit for consumption.

The details of the agriculture of cacao have been taken largely from Hart's work already referred to, supplemented and brought up to date by information supplied by personal friends engaged in cacao planting, and by the recent researches to be found in current journals issued by the Boards of Agriculture of Ceylon, Trinidad, and other cacao-producing countries.

Selection of site.—The best results will be obtained on a good loamy soil, of reasonable depth, with a moderate amount of lime and sand present, situated in a district where the seasonal fluctuations of temperature do not exceed the limits of 69° to 89° F.

A deposit of decaying vegetable matter, such as would be found on former forest soil, resulting from the fall of leaves and branches, is, of course, of great value, as a natural dressing of this sort would contain nitrogenous plant foods in a readily assimilable form, and would constitute a fine manure for a land where the subsoil did not show, on analysis, a sufficient wealth of plant nourishment.

Good drainage is most essential for the successful cultivation of cacao, as thereby the withdrawal of surplus and stagnant waters, both detrimental to cacao plantations, is assured.

The presence of salt in a soil is deadly to cacao, so that all situations likely to be affected by tidal waters should be avoided.

On the other hand, plantations situated high above the sea-level are not economical, owing to the lower temperature experienced at the higher elevation.

J. H. Hart* admirably sums up the qualities necessary

* J. H. Hart, 'Cacao,' 1900, 2.

for a perfect cacao plantation site as follows: "An ideal spot on which to found a cacao plantation is a well-sheltered vale, covered with large trees, protected by mountain spurs from the prevailing winds, well watered, and yet well drained, with a good depth of alluvial soil, on which rests a thick deposit of decayed vegetable matter, easy of access, and in a district distant from lagoons or marshes, for the sake of the proprietor's health. Such a spot in a climate similar to that of Trinidad could not fail to produce regular crops of the finest quality of cacao."

Selection of soil.—Close observations of a large number of analyses of soils suitable and unsuitable for the proper growth of the cacao tree, made by Professor Harrison in the Government laboratories of British Guiana, by Mr. Carmody, Government Analyst of Trinidad, and others, has led to the general conclusion that nitrogen, potassium salts, phosphoric anhydride and lime are absolutely essential to soils for cacao cultivation, while excess or deficiency of silica and silicates are detrimental.

The percentage of silica and silicates present are chiefly of importance owing to the effect which sand or silica has upon the mechanical state of the soil. A too great proportion means too light a soil, with too small a proportion of other useful components; a small percentage of sand and silica implies a heavy clayey soil. Analyses by the first experimenter show that good soils contain nitrogen from 0·1 to 0·309 per cent.; potassium oxide from 0·118 to 1·072 per cent.; phosphoric anhydride from 0·044 to 0·293 per cent.; lime from 0·356 to 4·981 per cent.

Poor soils contain nitrogen from 0·057 to 0·265 per cent. (usually about 0·1 per cent.); potassium oxide 0·029 to 0·109 per cent.; phosphoric anhydride from 0·002 to 0·157 per cent. (usually about 0·05 per cent.); lime from merest traces to 0·5 per cent. (in one isolated case 4·787 per cent.).

The suggestion that these four components of the soil

are of the greatest importance is verified not only by our knowledge of plant foods in general, but also by the analyses of the cacao tree, shoots, leaves and fruit, made by Marcano,* who estimates that an acre of twenty-year-old trees will contain 201 lb. of nitrogen, 95 lb. of phosphoric anhydride, 251 lb. of potash, and 400 lb. of lime.

These figures roughly show the composition of the existing tree and obviously do not represent specific amounts of components annually or occasionally extracted from the soil, but they clearly demonstrate the need of the existence of these four components if good and regular growth is to be made.

Chemical analysis of a soil alone is of little use to the agriculturist, for it is quite possible for land to possess all the ingredients requisite for the growth of any particular plant and yet be totally unsuited for its successful culture. The plant nourishment may be in a form unsuitable for root absorption, or, again, the mechanical nature of the soil may prevent the valuable part of the components being properly assimilated.

It is necessary, therefore, for the intending cultivator of cacao to take into consideration many other conditions of great importance, apart from the chemical composition, such as the mechanical state of the soil, natural drainage of the land, situation of the plantation with regard to light, air and winds, taken with which chemical analysis of the soil should be a most useful guide and added factor in determining the suitability of the land for cacao cultivation.

Selection of manure.—When the mechanical condition of the land is unsuitable, or from chemical analysis it is found that one or other of the necessary components is lacking, which will be evidenced by slow and retarded growth of the tree, production of few leaves, premature

* Marcano, 'Essai d'Agronomie Tropicale.'

falling of the crop, disease or blight, it will be necessary to make use of manures to correct and adjust the prevailing conditions.

It is impossible to teach in writing what manures should be used and how they should be applied, for there are many schools of thought, each claiming their suggestions of kind and application to be the most efficient.

Of chemical manures there is no end, but of all manures known, that from the farmyard is the one in which the cultivator places most reliance. The excreta from horses contain approximately 25 per cent. of solids, of which 3·5 per cent. is potash and soda, 0·4 per cent. phosphoric anhydride, and 0·6 per cent. nitrogen.

Such a manure, thoroughly blended with soil before planting the seed, and applied at the rate of 20 to 30 tons per acre, makes an admirable all-round dressing for cacao.

As it is probable that such a quantity of stable manure would not be easily obtainable for a plantation of large acreage, the judicious admixture of nitrate of soda, bone ash superphosphate, or dried blood, would enable the planter to reduce proportionally the quantity of natural manure.

Nitrate of soda has a tendency to cause a luxuriance of foliage; it also causes plants to grow thicker and mature earlier. It is most suited to clay soils, but owing to its solubility in water it cannot be economically applied before the crop is sown.

Bone ash superphosphate is also suited to clay soils and is intended to promote early maturity of crops.

Dried blood is most beneficial on light soils, and applied in fine powder, *per se*, at the rate of thirty to fifty bushels per acre, proves a most valuable manure for cacao trees.

Manures applied when the trees are in full growth should be carefully pricked into the soil about the roots, the greatest care being taken not to injure the branching

roots in any way, a precaution which cannot be too carefully observed.

The injury to the roots and the wounding of any other part of a growing tree gives access to fungus and wood parasites, and affords a means of escape of the stimulating juices which convey nourishment to every part of the tree. All injuries should be looked into with the greatest care, and a prompt dressing of tar and clay applied.

An interesting account of manures which have proved successful in cacao culture is given by Wright,* from whom the following results have been taken :

Country.	Nature of mixture.
Trinidad .	Basic slag, 4 cwt. per acre. Sulphate of potash, 1 cwt. per acre.
St. Lucia .	(1) Basic slag, 8 cwt. per acre. Sulphate of ammonia, 1 cwt. per acre.
,, .	(2) Basic slag, 4 cwt. per acre. Stable manure, 3 tons per acre. Sulphate of ammonia, 1 cwt. per acre.
Grenada .	(1) Basic slag, 8 cwt. per acre. Sulphate of ammonia, 1½ cwt. per acre.
,, .	(2) Basic slag, 8 cwt. per acre. Sulphate of potash, 1 cwt. per acre.
Dominica .	(1) Mulching with grass and leaves.
,, .	(2) Basic slag, 4 cwt. per acre. Sulphate of potash, 1½ cwt. per acre. Dried blood, 4 cwt. per acre.
Ceylon . .	(1) Lime and organic matter; the latter either as leaves or cattle manure.
,, . .	(2) Basic slag, 5 cwt. Ammonium sulphate, 200 lb.
,, . .	(3) Manures rich in readily soluble nitrogen and potash.

* H. Wright, 'Cocoa,' 1907, 180.

Cockran* gives the following blends of artificial manures as suitable for application to soils of known composition and found to be lacking in one or other of the necessary components:

I.

	Per acre.
Superphosphate of lime, 36 per cent. soluble	182 lb.
Sulphate of potash, 50 per cent. potash	120 ,,
Nitrate of soda	237 ,,
(Or sulphate of ammonia, 186)	

II.

Bone meal	300 ,,
Sulphate of potash	120 ,,
Castor cake	400 ,,

III.

Thomas's phosphate powder	360 ,,
Sulphate of potash	120 ,,
Castor cake	570 ,,

IV.

Thomas's phosphate powder	360 ,,
Sulphate of potash	120 ,,
Blood meal	300 ,,

V.

Fish manure	500 ,,
Bone meal	200 ,,
Sulphate of potash	120 ,,

VI.

Nitrate of soda	119 ,,
(Or sulphate of ammonia, 93)	
Blood meal	100 ,,
(Or castor cake, 200)	
Bone meal	150 ,,
Sulphate of potash	120 ,,

* M. Cockran, 'Report of Analysis of the Cocoa Tree Planters' Association of Ceylon,' 1898, 11.

Selection of seed.—Having briefly dealt with the sites, soils and manures most suited for cacao plantations, there remains the very important consideration of seed selection.

Cacao seed possesses but little vitality, and readily succumbs to dry air and alternations of periods of damp and dry weather, and it is therefore not easily sent to distant parts so as to be in a fit condition for germination at the end of the journey.

The planter should choose large seeds from *ripe* pods of trees which regularly produce the finest quality of beans. By this means, if the trees do not grow too close to others of inferior quality to run the risk of cross-fertilisation, the planter is more assured of a good, even, all-round crop.

The selection of the variety, Criollo, Forastero, or Calabacillo, must depend upon the soil and climatic conditions prevailing at the place chosen for the plantation.

From Criollo cacao are obtained the finest beans for flavour, but the crop is not so large nor the tree so hardy as the inferior-beaned Calabacillo. If the soil of the plantation is poor Calabacillo cacao will thrive the best, while the Forastero variety, occupying the intermediate position, will grow well in soils and climates where any cacao may be reasonably expected to flourish.

Hart has recommended the grafting of the finer quality Criollo to the hardier Calabacillo cacao, thereby obtaining the advantages of both varieties, and the additional benefit of being sure of obtaining a continual and even crop of the variety selected, which, by reason of possible cross-fertilisation of the flowers of the mother tree, is denied to trees grown from seed.

CHAPTER IV

THE AGRICULTURE OF CACAO

B. Planting, Diseases, Pruning, Picking

Planting.

The seed selected and the land prepared, it remains for the planter to decide whether he will place the seed direct into the land, when the position which the tree will take up will be permanent, or rear the seedlings in a nursery till their size and strength fit them to be transplanted to the open plantation.

In the former case the seed is carefully placed into the loosely broken ground, about 1 in. deep and 6 in. apart, in the form of a triangle, and a little light earth is sprinkled over them and gently trodden down with the foot. Each triangle is placed about 12 ft. apart.

As the trees grow and develop the weaklings are weeded out, making more room for the stronger-growing shoot to develop. It is a general rule that the higher the elevation of the plantation and the poorer the soil, the nearer may the trees be allowed to grow, a distance ranging from 12 to 15 ft. each way probably meeting all requirements.

It must be realised that no definite rule can be laid down for planting or for any other of the operations of the planter, which are necessarily only to be learnt by experience, but for a mental picture of a plantation the descriptions here given will serve.

PLATE II.

Photo, S. E. Jacobson.] [*Trinidad.*

CACAO TREES SHADED BY "MADRE DE CACAO," TRINIDAD. (See p. 29.)

In planting in nurseries the same system of sowing is employed, but added facility for individual and personal inspection is afforded. In the nursery the seedlings are tended until some two feet in height, care being taken that no direct heat from the sun should fall on the plants, a danger which is prevented both in the nursery and in the open plantation by shelters of either an artificial nature or trees which afford plenty of shade.

In Grenada and other hilly districts the formation of the land is taken advantage of for providing the necessary protection from the sun and wind, and in these places no trees are grown or artificial structures erected for that purpose.

In the lower lands of Trinidad open to the unchecked influence of the elements, protections from both wind and sun are erected and grown, shelters from the former being usually built outside the plantation, while shady trees are grown in rows side by side with the cacao. That protection from the sun was considered not only desirable but essential for the successful culture of cacao finds further proof in the fact that the principal and larger trees selected were usually those providing the greatest shade, and were seldom, if ever, of economic value.

Varieties of Erythrinas known as "Bois Immortel," or "Madre de Cacao" ("mother of cocoa"), to use the Spanish name, leguminous plants of dense shade (Pl. II), are most generally employed in Trinidad, and though from the nature of the plant it probably aids in accumulating nitrogen in the soil around the roots, its timber is quite useless even for fuel, and the boughs of the tree have the unfortunate characteristic of falling in wet and windy weather, with probable injury to the cacao growing beneath.

There are many other trees grown for the purpose of providing shade and especially favoured in different districts, among the smaller plants being Zea mays, castor oil,

cassava and banana or plantain, each of which provides seed fruit or root of some commercial importance.

It is noticeable, however, that until the rubber plant came into such prominence, the larger trees used for shading cacao were of little or no economic value.

The Heveas, from which Para rubber is obtained, are now largely used for shade, and, though comparatively slow growing, yield a produce of equal, if not greater, value than the cacao trees they shelter.

Appended is a list of shade trees commonly used in cacao producing countries: *

Adenanthera pavonina, *Albizzia moluccana*, *A. Lebbek*, *A. odoratissima*, *A. stipulata*, *Erythrina lithosperma*, *E. umbrosa*, *E. Indica*, *E. ovalifolia*, *E. velutina*, *Artocarpus integrifolia*, *A. nobilis*, *Cassia Siamea*, *Casuarina equisetifolia*, *Eugenia Jambos* (*Jambo*), *Filicium decipiens*, *Melia dubia*, *Mesua ferrea*, *Pithecolobium Saman*, *Castilloa elastica*, *Manihot Glaziovii*, *Hevea brasiliensis*, *Gliricidia maculata*, *Pterocarpus indicus*, *P. marsupium*, *Vateria acuminata*, *Acacia pycnantha*, *Cedrela serrata*, *C. Toona*, *Eucalyptus leucoxylon*, *E. marginata*, *Grevillea robusta*, *Michelia Champaca*, *Myristica laurifolia*, *Azadirachta indica*, *Peltophorum ferrugineum*, *Swietenia macrophylla*, *Tamarindus indica*, *Thespesia populnea*, and others.

Other plants which, whilst providing a certain amount of shade, are grown for their commercial value as inter- or catch-crops between the cacao trees, are—Lemon grass, citronella, cotton, groundnuts, cassava, chillies, pepper, bananas, yams, coffee, tobacco, rubber, tea, camphor and coconuts.

Diseases.

A matter of no small importance to be considered in selecting shade trees is their immunity from disease.

* Vide also H. Wright in 'Cocoa,' 1907.

As a general rule it may be stated that the cacao tree is not subject to the attack of parasitic fungi, but ill-drainage of the land or close proximity to other trees affected with fungoidal disease may speedily bring about an epidemic in the plantation.

"Canker" and "black rot" are the two most deadly diseases to which cacao is prone. The former is due to a fungus allied to *Nectria*, which attacks the bark of cacao and other trees, and which has now been named *Nectria Bainii*. The latter also is due to a parasitic fungus similar in many ways to the "black rot" of potato, *Phytophthora infestans*, and to *Peronospora* generally, and which has been named *Phytophthora omnivora*.

"Black rot" attacks the cacao pods, sending its filaments well into the interior of the pod, which in time is turned into a black pulpy mass, while the fungus appears on the outside surface of the shell as a white mould. This fungus has been identified in cacao plantations in all districts, especially Ceylon and Trinidad. There is little doubt that it was *Phytophthora omnivora* which destroyed the crops and prosperity of Trinidad in 1727, a disastrous episode already mentioned as being reported in De Verteuil's book on Trinidad.

A new disease appearing in the West Indian cocoa plantations was noted by Bancroft* last year. The parasitic fungus belongs to the genus *Colletotrichum*, and has previously been recorded from other cacao-producing centres, though this seems to be the first appearance in the West Indies. It has been mentioned by Hall and Drost,† Delacroix,‡ and von Faber,§ in their studies on fungi parasitic on plants, and besides being extremely conta-

* C. K. Bancroft, 'W.I. Bulletin,' 1910, xi, 34.

† Hall and Drost, 'Recueil des Trav. Bot. Néerl,' 1908, iv, 343.

‡ Delacroix, "Champignons parasites des plantes cultivées dans les regions chaudes," 'Bull. de la Soc. Myc. de France,' 1905, xxi, 191.

§ F. C. Von Faber, 'Die Krankheiten und Parasiten des Kakaobaumes,' 1909.

gious, causes complete deterioration of the pods, making them hard and woody and sapping the juices which protect and nourish the beans.

The considerable decrease in the yield of the 1906 crop in Ceylon, as compared with that of 1905, was attributed by Sir W. Ward, then Consul-General at Hamburg, in an article to the 'Grocer and Oil Trade Review,' January, 1908, to the prevalence of disease in the plantations of that island.

The suggested remedies are such as would be applied to any tree suffering from disease, namely, the strengthening of plant growth by addition of manure to the soil, installation of a proper drainage system, and the removal of all possible means of contamination by lopping off the diseased branches of affected trees and a complete destruction by fire of the refuse thereby created.

It is not an uncommon practice for the pods to be shelled on the plantation itself for the removal of the beans, the husks being allowed to rot on the surface of the land until sufficiently decayed to be dug in.

This practice constitutes a danger of spreading disease among the cacao trees, and it is most essential that all affected husks should be removed outside the plantation and burnt forthwith. A check on disease may often be brought about by the use of sprays of solutions containing sulphate of iron or copper, fungicides which have proved most efficacious in combating the potato "black rot" and "corn smut" (*Ustilago carbo*) in this country.

Among the insect pests mentioned by Hart as causing the greatest trouble to cacao planters are the parasol "ants" (*Æcodoma cephalotes*) and the "cacao beetles" (*Steirastoma histrionica*).

The "ants," which remove portions of the cacao leaf as a foundation apparently for the growth of certain fungi, upon the conidia of which they feed, are most persistent in

their depredations, and in spite of sulphur or tobacco fumes will often recur at the sites of their former nests.

So much damage has been done in the past to plantations by the ravages of these "ants" that the Legislative Council of Trinidad can pronounce any district troubled with the pests to be in quarantine.

The "cacao beetles" deposit their eggs in the bark and wounds of the tree, and, by boring small holes through the branches, cause boughs to fall in windy weather.

The most satisfactory cure for this pest seems to be the cutting away and burning of infected parts or the more cautious probing to remove the beetle; in either case the wounds in the tree must be dressed with tar and clay or other antiseptic mixtures.

The aphis fly and lice common to all vegetation are to be found on the cacao tree, and though no real harm is caused by their presence, the cleanly planter will endeavour to keep them away by spraying and other preventive measures.

Vegetable parasites and orchids, words used indiscriminately in Trinidad for one and the same thing, are many, and have been described in articles submitted to the Association of German Chocolate Makers.

There is little doubt that all such cancerous growths sap the energy of the tree, and should be removed at the earliest opportunity by cutting as close as possible to the point of juncture.

Pruning.

Parasites and the seeds of disease fall upon the tree under most favourable conditions for their growth, when the sap is down and the dead wood abounds. It is a mistake, however, to cut away all the old wood at once, as heavy pruning always stays the growth of a tree by

reason of leakage of sap, which must occur when incisions are made.

The object of pruning is primarily to produce an even, symmetrical tree with plenty of foliage and fruit, to remove boughs which are past bearing, and to induce new growth.

In young trees with a single shoot, three, or at the most four, small branches should be allowed to form at the sides with as much regularity as circumstances will permit.

In the same way, by judicious pruning, the secondary and tertiary branches should be induced to grow at regular intervals.

In the early stages the wood should be pruned when in a state to be "pinched" and not cut, and whenever a knife is employed the greatest care should be taken that ragged cuts are not made.

Later, when knife and saw are brought into use, symmetry, removal of the oldest wood and encouragement of young shoots in the most desirable positions, should be aimed at, and the wounds made should be covered with some antiseptic mixture.

Pruning is best carried out at the close of a crop, when both flower and fruit are absent, and though it is often desirable and necessary to prune whilst the crop is on the trees, care must be exercised lest injury occur to the fruit, and, more essential still, to the flower of the next season's fruiting.

Picking.

When the trees are three or four years old they commence to flower, and, after they have once produced fruit, regular crops may be expected for fifty or more years if proper care is taken.

The fruit, which has already been described, is gathered,

PLATE III.

Photo, S. E. Jacobson. [Trinidad.

Picking the Cacao Pods, Trinidad. (See p. 34.)

when in reach, by means of a hand knife, the cacao hook or pruning knife, fitted to the end of a long stick or bamboo, being used for gathering the fruit on the higher branches (Pl. III).

The flowers for the following crop usually occur at the point of juncture of the fruit with the tree; consequently the picking or cutting is attended by considerable risk, and it is important that the cut should not be made too near to the main support.

Colour and sound on tapping are the most sure guides to the planter as to whether the pod is ripe for picking, but it is admitted on all sides that great experience must be acquired before absolute certainty as to the ripeness of a pod can be ascertained by these means.

For this reason picked men of experience should be selected for gathering the fruit, as the beans of unripe or over-ripe pods, if not discarded, will lower the standard of the bulk.

If only ripe pods are gathered, the sorting which they must undergo is greatly simplified, and the planter has the satisfaction of obtaining his cacao in the finest condition.

CHAPTER V

FERMENTATION OF THE BEANS

Fermentation, which has been looked upon from very early times as a necessary process for obtaining cacao of finest aroma and flavour, may be regarded primarily as the most convenient method of removing adhering pulp, and of obtaining the bean in a suitable state for quick drying.

It is undoubtedly true that the cacao commanding the highest market price is usually fermented, so that a good deal may be said for the first argument in its favour. However that may be, the difficulty of removing the pulp clinging to the beans and of rapidly drying the cleaned article without allowing germination to commence would be most difficult if fermentation were not resorted to.

Germination of the bean would entail a loss of a certain amount of fat, but, by quickly killing the embryo and life of the seed by fermentation or sweating before the more readily assimilated sugars are used up, this valuable portion of the bean is preserved.

The changes which go on during fermentation will be considered more fully later in this chapter, when the results of analyses of beans before and after fermentation are dealt with, and for the present it will be assumed that improvement of the kernel and ready removal of adhering pulp are the main objects for which fermentation is employed, the reason why such improvements or advan-

PLATE IV.

Photo, S. E. Jacobson.] [*Trinidad.*

OPENING THE CACAO PODS, TRINIDAD. (See p. 37.)

tages are obtained by the process being discussed as necessity arises.

The pods, after they are picked, are sorted into grades according to their quality, the over-ripe, under-ripe, or diseased being put on one side.

The grading completed, the pods are "broken," either in the plantation or in the fermenting house, the latter place being preferable owing to the possibility of the decaying husks conveying disease to the trees if allowed to remain in the plantation.

The shelling or breaking is performed by a cut with a knife on one side of the pod, which is then broken open with the hands (Pl. IV), or the more primitive method of dashing the pods on a log of wood, as employed in Nicaragua, may be resorted to.

The beans and pulp are removed from the broken pods, and conveyed to the sweating house, where they are allowed "to stew in their own juice"* in vats (Pl. V), until they have assumed the cinnamon red colour so much desired.

The exact condition to which the beans must be brought by fermentation is known only to the practical planter, but whether the process is carried out in vats, as in Trinidad and Ceylon, or fermentation is allowed to proceed in the beans packed warm from the sun in sacks, as is the custom of the small grower in Venezuela, the results achieved are the same in their most essential points.

In order to fully appreciate what takes place during fermentation, it is first necessary to know the composition of the materials taking part in the process.

Professor Harrison has made careful analyses of the pulp and beans before and after fermentation, and though it will be unnecessary to quote in full all his results, the

* Dr. Chittenden in Prize Essay on Fermentation of Cacao, 'Agricultural Record,' 1890.

following collected figures will give all the information necessary :

TABLE II.—*Changes taking place in the Kernel of the Beans of "Calabacillo" during Fermentation and Curing.*

	Fresh beans.	Fermented and cured beans.	Loss during fermentation and curing.
Water	37·637	3·675	33·962
Albuminoids	6·696	4·419	2·277
Indeterminate nitrogenous matters	0·531	2·059	1·521
Theobromine	1·352	1·003	0·349
Caffeine	0·108	0·032	0·076
Fat	29·256	29·256	*Nil.*
Glucose	0·991	0·604	0·387
Sucrose	Trace	*Nil.*	—
Starch	3·764	3·221	0·543
Astringent matters	5·004	3·610	1·394
Pectin, etc.	0·657	1·178	+0·521
Cacao red	2·952	1·390	1·562
Digestible fibre	5·112	3·737	1·375
Woody fibre	3·030	2·780	0·250
Tartaric acid (free)	0·079	0·328	+0·259
Acetic acid (free)	*Nil.*	0·544	+0·544
Tartaric acid (combined)	0·477	0·377	0·100
Iron peroxide	0·032	0·069	+0·037
Magnesia	0·324	0·375	+0·051
Lime	0·054	0·118	+0·064
Potash	0·842	0·592	0·250
Soda	0·239	0·288	+0·049
Silica	0·016	0·022	+0·006
Sulphuric anhydride	0·079	0·031	0·048
Phosphoric anhydride	0·749	0·712	0·037
Chlorine	0·019	0·012	0·007
	100·000	60·442	

TABLE III.—*Composition of Sweatings taken from the Runnings of Sweating Boxes, and of Original Pulp.*

	Sweatings.	Original pulp.
Water	84·817	83·030
Albuminoids	0·062	1·271
Indeterminate nitrogenous matters	0·250	*Nil.*
Glucose	11·604	0·091
Sucrose	0·638	1·001
Astringent matter, etc.	0·354	0·108
Alcohol	0·180	*Nil.*
Tartaric acid (free)	0·340	0·606
Acetic acid (free)	0·892	Trace
Acetic acid (combined)	0·290	—
Iron peroxide	0·038	0·010
Magnesia	0·074	0·073
Lime	0·029	0·030
Potash	0·354	0·248
Soda	0·004	0·015
Sulphuric anhydride	0·021	0·031
Phosphoric anhydride	0·038	0·098
Chlorine	0·007	0·061
	100·000	
Tartaric acid (combined)		0·351
Theobromine		0·348
Caffeine		0·059
Fat		0·421
Starch		1·305
Pectin, etc.		1·126
Cacao red		0·705
Digestive fibre		6·564
Woody fibre		2·455
Silica		0·003
		100·000

The beans and their adhering pulp during the process of fermentation rise in temperature from 30° to 40° C. in about three days, finally reaching 48° or 49° C. if a good fermentation has been secured. The fermenting mass should never be allowed to reach a higher temperature than 60° C., and in order to prevent this frequent turning of the beans is necessary.

Preyer,* in an article on cacao fermentation, states that the micro-organisms engaged in the operation attack the husk and kill the embryo, whilst the soluble matters and enzymes diffuse through the dead tissue. According to this writer the fermentation should be stopped when the outer skin is loosened, so as to be readily removable in a subsequent washing process. The same author states that the yeasts isolated from the vat liquors during a Ceylon fermentation consisted of budding fungi, similar to *Saccharomyces ellipsoideus* and *S. membranæfaciens* and a new species which he named *S. theobromæ Preyer*, to which he attributes special activity.

The whole process of fermenting and curing may occupy from nine to twelve days, though three days may be sufficient for the first operation if fermentation starts at once under ideal conditions of temperature. After the process the skin of the bean is found to be shrunk and toughened, and in a fit state to withstand fungoidal growths, the kernel being changed from its somewhat purplish hue to a rich brown and the bitter and astringent taste greatly modified.

Briefly, the changes which take place in the operation of sweating are as follow:

The beans and pulp exposed to the air are at once attacked by a yeast fungus, *Saccharomyces theobromæ Preyer*, which causes a rise in the temperature of the materials due to the chemical action of breaking up the

* Axel Preyer, 'Woch für Brau,' 1901, xviii (21), 277, and 'Der Tropenpflanzer,' 1901, v.

PLATE V.

Photo, S. E. Jacobson.] *Trinidad.*

SWEATING BOX, TRINIDAD. (See p. 37.)

sugary matters subjected to its influence, with the production of alcohol.

Later, acetic acid fermentation is set up by the intervention of a fungus growth, *Mycoderma aceti*, which speedily attacks alcoholic liquids exposed to air. Another increase in temperature is noticed with the second reaction, and so much heat is developed that alcoholic fermentation is practically stopped. Both the alcoholic and acetic acid fermentations are due to the activity of the enzymes or juices secreted by the growing fungi, and it must be inferred, from the analyses given, that other fungi possessing proteolytic or albuminoid splitting enzymes are also actively engaged in obtaining the general result of the fermentation process.

The loss of starch from the bean during fermentation must be attributed to the diastase content of the saccharomyces, as observed by Pfeffer,* or to the diastase of secretion which all seeds contain, and which plays so important a part in providing soluble nourishment for the growing plant during the germination of the seed.

To recapitulate in proper sequence, the process of fermentation is as follows:

(1) Conversion of starch into soluble dextrin and sugar by means of diastase, an operation which would take place naturally at the commencement of fermentation process, even if no saccharomyces were present.

(2) Some of the sugars of the pulp and the original and newly formed sugars of the beans are next converted into alcohol by the sugar-splitting enzymes of the saccharomyces, with a consequent rise of temperature.

(3) The alcohol so formed rapidly undergoes fermentation by the agency of *Mycoderma aceti*, with a still further rise of temperature. At the same time there occurs a loss

* Pfeffer, 'Ueber die regulatorische Bildung von Diastase.'

of albuminoid matter, both in the pulp and bean, attributable to the action of proteolytic ferments.

The chemical action during the process of fermentation has the effect of withdrawing the soluble matters contained in the kernel to the liquid running away from the fermenting mass, and consequently the quantities of the soluble mineral matters, chiefly consisting of potash and phosphoric acid, are found to be considerably reduced in the fermented beans and increased in the sweatings.

The astringent matters, to which the acrid taste of the fresh beans are due, are undoubtedly hydrolysed during the fermentation, as they are found by analysis to be in greatly reduced proportions both in the fermented pulp and beans.

In the case of the Calabacillo bean, the loss during fermentation and curing is 62·5 per cent., of which 59·0 is water and 3·5 organic and mineral matters.

Loss of alkaloids, gums, vegetable fibre, astringent matters and cacao red occur in the beans during fermentation, beside the more apparent losses in sugars, starch and albuminoid matters, the only gain of real importance being in acetic acid, the result of fermentation, and certain mineral matters which may be attributed to the accumulation of dirt.

In later analyses by Prof. Harrison of a mixture of beans containing one fifth Calabacillo and four fifths Forastero varieties before and after fermentation and curing, the losses and gains of the beans during the process are still more marked, the latter being entirely confined to 0·257 acetic acid, 0·010 iron peroxide and 0·010 silica, while the total loss amounted to 64·062 per cent., of which 56·419 was water, 0·429 sucrose, 1·280 starch, 0·301 glucose, 1·258 astringent matter, 0·982 albuminoids, 1·167 digestible fibre, and 0·270 cacao red.

The following results, collected by Preyer,* as to the temperature of fermentation in different districts, stated by various observers, are of interest:

	Method of fermentation.	Temperature employed.
Preyer . .	Heaping method (Ceylon).	
	In the upper half . . .	30–40° C.
	In the lower half . . .	Outside temperature to 30° C.
Chittenden .	Some samples fermented well at .	26·7° C.
,, .	With the method in vogue in Trinidad	46–49° C.
Morris . .	By the method practised in the West Indies	About 60° C.
Strickland .	Three-tank system (West Indies):	
	In tank 1	Not over 46–49° C.
	In tank 2	Not under 35° C.
	In tank 3	,, ,, ,,
Friederici .	Three-tank system (Cameroon):	
	In tank 1	30–33° C.
	In tank 2	35–38° C.
	In tank 3	Not over 43–45° C.
Preuss . .	Three-tank system (Surinam) . .	Never above 45° C.
Wright . .	Three-tank system (Ceylon):	
	Tank 1	25–30° C.
	Tank 2	30–40° C.
	Tank 3	33–44° C.
Johnson . .	Heaping method (Gold Coast) . . .	Below 60° C.

For further information on fermentation temperatures the author recommends Wright's book on cocoa already mentioned, and which contains fullest details, both on the different methods of fermentation practised and on the various results so obtained.

* A. Preyer, 'Über Kakao-Fermentation,' 6.

CHAPTER VI

PREPARATION OF THE BEANS FOR MARKET: WASHING, DRYING, FINISHING, OR POLISHING

Washing.

After fermentation is complete, and the required colour and aroma of the beans obtained, the cacao should be submitted to washing at once, if at all, otherwise fermentation will proceed beyond the desired limits.

No harm whatever can come to the cacao by washing from the points of view of the chocolate manufacturer and consumer, though the loss of weight attendant to the process due to the removal of adhering pulp may be imagined by the planter to be a matter of considerable importance, and will frequently cause him to forego the operation, in which case the period of fermentation must be somewhat curtailed. Cleaned beans will always command the higher price, and in these days of scientific enlightenment there is little to be gained by the planter in neglecting to wash the cacao, since the absolute yield or weight of the kernel, apart from the skin and its adherent dirt, is as important a factor in determining market value as the quality of the kernel itself.

The beans are placed in sieves or troughs, and thoroughly stirred and scrubbed under water till all adhering organic matter is removed and the beans are clean and smooth, when they are ready for drying.

PLATE VI.

Photo, S. E. Jacobson.] [*Trinidad.*

ARTIFICIALLY DRYING CACAO, TRINIDAD. (See p. 45.)

Drying.

The method adopted for drying may be by exposure of the washed cacao to the heat of the sun, or by a system of hot water or steam pipes under cover if the climate does not lend itself to the natural process (Pls. VI and VII).

In Trinidad the beans, which are not always washed, are exposed to the heat of the sun on open wooden floors or trays, which are covered up when it rains, either by a movable roof or by placing the trays under a fixed shelter.

In Ceylon the washed beans are dried either artificially or by the sun's heat as slowly as will allow the danger of the formation of mould to be avoided, a process which is accelerated without injury to the quality of the cacao if proper fermentation has been accomplished.

The beans, which are usually spread on the drying floors to a depth of three or four inches, must be kept constantly turned to prevent local over-heating, and to enable a circulation of air to reach all parts of the layers.

There does not seem to be any chemical principle underlying the theory of slow drying, but since it is adopted in all cacao-producing countries it must be assumed that there is some value in the restriction, and it is highly probable that more even and good-looking samples are obtained than when the beans are dried off quickly.

Finishing.

In order to accelerate the drying of the beans without applying extra heat, and especially during the damp weather, the planters of Trinidad, Venezuela and certain other countries make use of fine dried earth, which they sprinkle over the beans and intimately mix in with the drying mass (Pl. VIII).

This provides a ready method of removing any

remaining pulp, as the drying beans are frequently raked over, and the friction of rubbing one against the other soon causes the adhering matter to fall away.

Other purposes which are served by this treatment are an improved finish in the appearance of the beans, protection against mould, and additional weight.

With regard to these secondary advantages, the beans, treated with red earth or clay, which is usually employed, certainly present a brighter and cleaner appearance, and the mineral covering so formed provides additional protection against mould and fungus growths so feared by the cacao planter, and which frequently necessitate the beans being dried for two or three days beyond the time usually allowed by the planter for complete drying. There can, however, be no real advantage to the planter in adding weight to the beans.

Polishing.

In certain countries, even where the use of earth is customary, the fear that mildew should attack the drying bean is so great that a process of hand rubbing or "dancing" is employed (Pl. IX).

Dancing consists of treading the layers of drying beans with the naked feet, and, as with hand rubbing, serves the double purpose of removing the mildew from the bean by friction against one another, and of giving a finish or polish.

It is difficult for anyone but an experienced person to say when the cacao has received sufficient drying, but from analyses of the unroasted shells and kernels* of beans bought on the market, it would appear that the cacao may be considered sufficiently dry when the moisture content of the shells has been reduced so as not to exceed 13 per cent., and of the kernels 8·5 per cent.

* Zipperer, 'Untersuchungen über Cacao, etc.,' 55, 56, 57.

PLATE VII.

Photo, S. E. Jacobson.] [*Trinidad.*

CACAO BEANS DRYING IN THE SUN, TRINIDAD. (See p. 45.)

RESUMÉ OF CHAPTERS III TO VI INCLUSIVE. IMPORTANCE OF NATURAL CONDITIONS AND PROCESSES OF FERMENTING AND CURING ON QUANTITY AND QUALITY OF THE FINISHED CACAO.

Natural Conditions.

Site, soil, and seed play very important parts in determining both the quality and quantity of the resulting beans, inasmuch as they constitute those natural conditions which regulate the production of good healthy crops of fixed varieties of cacao.

The site must be one sheltered from prevailing winds and shaded from the direct rays of the sun, both conditions being accomplished by selecting a plantation in the shadow and under the lee of high hills or mountains, or by erecting artificial shelters and growing shade trees to serve the double purpose.

The soil should be of good light loam, of reasonable depth, and should contain sufficient quantities of nitrogen, lime, potassium salts, and phosphoric anhydride.

Good drainage and freedom of the soil from salt are most essential to the successful culture of cacao.

In the absence of any or all of the necessary components of the soil, manures, to supply the deficiency, may be applied. Stable manure when obtainable is most to be be recommended for its safe application and efficiency.

If these conditions of site and soil are observed in districts where the temperature never falls below 69° F., and which possesses a normal rainfall, a good acreage yield is assured.

The seed is one great factor in determining quality, and may be chosen from Criollo, Forastero, or Calabacillo varieties of cacao.

Criollo cacaos have the finest quality beans, but the trees are not hardy, and can only be successfully grown under the best conditions of climate and in the richest of soils.

Calabacillo cacaos are the strongest growers and can be made to succeed in very poor soils, but the beans are of inferior quality, and never command the highest market price owing to their astringent and bitter taste.

Forastero cacaos occupy an intermediate position between Criollo and Calabacillo, and may be expected to flourish wherever cacao can be reasonably expected to grow.

Hart recommends the grafting of Criollo on to the Calabacillo variety, thus obtaining the finer qualities of both kinds and ensuring a regular crop of beans of constant species.

Pruning is necessary for production of luxuriant foliage and good yield of fruit, but where incisions are made antiseptic dressings should be applied to the wounds in order to prevent access to parasitic fungi and insects.

Disease may be avoided by keeping the trees healthy and strong and by paying attention to the soil of the plantation and the proximity of diseased shade trees, and may be held in check by spraying the affected parts with solutions of sulphate of copper or iron. After shelling, the pods should not be allowed to rot within the precincts of the plantation, and all diseased branches, pods, and other parts of the tree should be burnt.

In picking, care should be taken to prevent injury to the flowers of the next crop, which occur at the point of juncture of the pod with the tree, and that only ripe pods are picked if the finest quality cacao is required.

Shelling should be conducted so that no injury occurs to the enclosed beans, and that no diseased pods be allowed to rot near the plantation.

PLATE VIII.

Photo, S. E. Jacobson. [*Trinidad.*

CLAYING CACAO, TRINIDAD. (See p. 45.)

Processes of Fermenting and Curing.

Fermentation commences with the conversion of the starch by diastase into soluble starch and sugar, followed by alcoholic and acetic fermentations which reduce the proportion of sugars in the bean.

During fermentation the beans lose a certain amount of moisture, albuminoid matters, alkaloids, gums, fibrous matters and cacao red, besides the greater losses of starch and sugars.

The best temperature for fermentation is about 49° C., and 60° C. should never be exceeded.* The whole process may occupy from nine to twelve days, though three days may be sufficient under ideal conditions.

The most obvious advantages gained from the process of fermentation and curing are: (1) The improvement in the quality of the kernel by loss of astringent matters; (2) the modification of the purple colour of the kernel from purple to a fine cinnamon brown; (3) the rendering of greater facility for the removal of adhering pulp, enabling the beans to be more quickly dried; and (4) the toughening of the skin of the bean so as to make it more impervious to mildew.

After fermentation it is advisable to wash the beans immediately to prevent further action, and to so regulate the drying that the maximum time is taken without risk of the formation of mildew.

It seems to be unanimously agreed that slow drying is desirable, though no chemical explanation is forthcoming.

To prevent mildew from attacking the drying beans it is customary to many countries to sprinkle fine dry earth

* Preyer in 'Der Tropenpflanzer,' 1901, v, points out that in Ceylon the most favourable temperature for fermentation is 38° C., above which inferior results are obtained. This, however, does not seem to be universally accepted as the "optimum" temperature. *Vide* also Chapter V, p. 43.

upon them, usually of a red and ferruginous nature. This operation also gives a better appearance to the beans and removes the remains of any adhering pulp.

In some countries "hand rubbing" or "dancing" is employed to remove mildew from the drying beans by friction one with the other, and to give a fine polished appearance to the cacao.

PLATE IX.

Photo, S. E. Jacobson.] [*Trinidad.*

"DANCING" THE CACAO, TRINIDAD. (See p. 46.)

CHAPTER VII

CHARACTERISTICS OF THE PRINCIPAL KINDS OF COMMERCIAL CACAO BEANS

In the foregoing chapters it has been shown how the appearance of the beans prepared for market is affected by the variety of cacao grown, and the varying systems of fermentation, drying, finishing and polishing employed in the different cacao-producing districts.

By means of these external differences in the finished beans it is possible for the purchaser to tell, with practice, the land of their origin, and taking into consideration the appearance and flavour of the internal kernel, to determine the nature of the variety of cacao and the processes which it has undergone.

In considering the descriptions of the beans which follow it must be borne in mind that "blends" may be met with on the market, and that seasonal differences, especially during the harvesting of the bean, may be responsible for variation in appearance and flavour from the general characteristics here given.

The cacaos on the market are of either American, West Indian, African or Asiatic origin. American cacaos include those from Ecuador (Esmeraldas, Guayaquil Ariba, and Guayaquil Machala); Venezuela (Socunusco, Caracas, and Puerto Cabello); Surinam (Maracaibo, Berbice and Essequibo); Brazil (Maranhão and Bahia), Cuba and Porto Rico.

The cacaos of most importance derived from the West

Indies include those of Haiti, Trinidad, San Domingo, Grenada and Jamaica.

From Africa come the cacaos of San Thomé, Cameroon, the Gold Coast, and Congo Free State.

The Asiatic cacaos of most importance are from Ceylon and the Dutch East Indies (Java).

American Cacaos.

Ecuador (1906 output, 23,856 tons).

1. *Esmeraldas.*—Beans: Small, heavy, plump, olive-shaped. Shell: Yellow-brown. Kernel: Dark violet; of mild and fine flavour. It is said that the finer sorts of this bean are never imported into Europe, as the production is small and the crops are, for the most part, consumed in the country of their origin.

2. *Guayaquil Ariba.*—Beans: Large, flat, wide, irregular. Shell: Covered with yellow-brown earth. Kernel: Pale violet, with white, dusty surface; slightly bitter and strong, of scented aroma. These beans being of a strong flavour are usually blended with milder and finer quality of cacaos, and are much used for English and German chocolate making.

3. *Guayaquil Machala.*—Beans: Flat and irregular. Shell: Covered with red earth. Kernel: Dark brown colour; bitter to the palate. Germany is a large consumer of these beans. In 1909 the output of cacao from Guayaquil constituted 90 per cent. of the total output of Ecuador,* which stood second on the list of cacao-producing countries for that year, with a production of 30,358 tons, a considerable increase on 1904. About 10,000 tons of this variety was imported into France in 1909.†

* 'Tea and Coffee Trade Journal,' May, 1910.

† *Loc. cit.*

PLATE X.

[*Photo, S. E. Jacobson.*]

[*Trinidad.*

SORTING CACAO BEANS ON A DRYING FLOOR, TRINIDAD.

Venezuela (1904 output, 13,048 tons).

1. *Soconusco, or Royal Soconusco.*—Beans: Small, plump, olive-shaped; slightly larger than Esmeraldas. Shell: Dirty yellow colour, loose; lighter than Esmeraldas. Kernel: Violet red colour; fine mild flavour.

2. *Caracas or Mainland cacao.*—Beans: Irregular, olive-shaped. Shell: Thick (about 15 per cent. of the weight of the bean); covered with smooth, reddish-brown earth. Kernel: Pale brown colour; contains about 50 per cent. fat; fine flavour. There are two grades of Caracas cacao, large and small, and, according to the names under which they are sold in France, are classified as follow: (*a*) Chuao, (*b*) Occunare, (*c*) Choroni, (*d*) Puerto Cabello, (*e*) Guiria, (*f*) Carupano, (*g*) Rio Caribi, (*h*) La Guayra or Rio Chico. These names are derived either from their place of origin or from the port whence they are shipped. This class of bean is used for the finest European chocolates, and is frequently blended with Trinidad or other milder cacao owing to its exceptionally strong and characteristic flavour. An increasing output of Venezuelan cacao is shown, the figures for 1909 amounting to 16,968 tons, of which 60 per cent. went to France.

Surinam (1904 output, 854 tons).

1. *Maracaibo* (Columbia).—Beans: Medium size, irregular; similar in appearance to Caracas. Shell: Smooth; covered with reddish-brown earth. Kernel: Reddish-brown colour; harsh to the palate; rich in fat. The cultivation of Maracaibo cacao is small, and the beans are seldom met with in the European markets. It is customary, when used, to blend this variety, as is the case with British Guiana cacaos also, owing to their richness in cacao fat and their strong flavour.

2. *Berbice* (British Guiana).—Beans: Small, irregular.

Shell: Covered with greyish earth; easily separated from the bean. Kernel: Dark brown colour; rich in fat; harsh and smoky to the palate.

3. *Essequibo* (British Guiana).—Beans: Large, close, oval; larger than, but similar in every other way to Berbice variety. Beans from Dutch Guiana and two other distinct varieties are occasionally met with in European markets. Holland is the chief consumer of the cacao from Dutch Guiana. The output of Surinam cacaos for 1906 was 1,457 tons,* as compared with 854 tons for 1904.

Brazil (1904 output, 23,160 tons).

1. *Maranhão* (*Maranon or Maragnan*). — Beans: Medium size and quality; elongated and flattened. Shells: Usually red-brown. Kernel: Light brown to dark red; rich in fat; of a mild flavour when gathered ripe, frequently bitter, harsh and mouldy to the palate, owing to their being picked when still unripe.

2. *Bahia.*—Beans: flat, irregular. Shell: Ranging from dirty grey to rich brown, according to the extent of fermentation. Kernel: Usually dark violet; bitter. England is a large consumer of Bahia cacao, as also in Switzerland. Maranhão and Para beans do not figure on the English market, being chiefly consumed by the French chocolate makers. Brazil cacaos show an enormous increase in production in the last few years. The 1909 production amounted to 33,036 tons, of which one third went to Germany, 7,589 tons to France, and about 3,000 tons to the United Kingdom. H.M. Consul at Bahia, Mr. D. R. O'Sullivan,† states that Bahia is capable of largely increasing its output of cacao, of which there are three varieties, Cacao Para, Cacao commun, and Cacao

* Sir W. Ward, H.M. Consul General at Hamburg, in 'The Grocer and Oil Trade Review,' January, 1908.

† 'The Public Ledger,' April, 1909.

Maranhão, but that an inadequate railway system does not present facilities for transport to the planter. Experiments made on the artificial drying of Bahia cacaos have recently resulted in a great improvement in the quality of these beans, the artificially dried or "estufa" cacaos commanding a higher price on the Bahia market than those dried in the sun.

3. *Cuba and Porto Rico* (1904 output, 3,266 tons).—Beans: Flat, irregular. Shell: Not easily detached from the kernel; frequently found with dried pulp adhering. Kernel: Dark violet colour; usually harsh and of poor chocolate flavour when roasted. The production of Cuban cacaos does not show any appreciable increase in late years.

West Indian Cacaos.

1. *Haiti* (1904 output, 2,531 tons).—Beans: Flat and egg-shaped; of poor quality. Shell: Brown and clean. Kernel: Dark brown; slightly bitter to the palate. Haiti or Port au Prince cacaos are smaller than, and of inferior quality to, the Mainland products. In 1906 no increase in production of Haiti cacaos over former years was notified.

2. *Trinidad* (1904 output, 18,574 tons).—Beans: Large, broad, flatter than Caracas. Shell: Greyish brown; readily detached, loose. Kernel: Usually dark brown; inferior qualities pale brown; pronounced fine flavour. Trinidad cacaos, which include the three varieties, Criollo, Calabacillo, and Forastero, are all used largely by English chocolate manufacturers. Trinidad showed a decrease in output in 1906, with a total of 12,956 tons, but increased in 1909 considerably over the 1904 output, showing a total of 22,768 tons, of which 40 per cent. went to the United States.

3. *San Domingo* (1904 output, 13,557 tons).—Beans: Flat, irregular. Shell: Red-brown. Kernel: Dark blue violet with paler fracture; slightly bitter to the palate. In 1906 the output of San Domingo cacaos reached 14,387 tons, falling to 14,286 tons in 1909.

4. *Grenada* (1904 output, 6,226 tons).—Beans: Smaller, but similar to Trinidad. Shell: Pale brown; usually loose and moist to the touch. Kernel: Harsh, bitter; frequently of a winey or fermenting flavour. Cacaos from Martinique and Guadeloupe (united 1904 output, 1,215 tons) show similar characteristics to Grenada product, and though somewhat redder in appearance the beans have the same raw and harsh flavour. A decreased output to 4,978 tons was noticed for Grenada cacaos in 1906; in 1909 an increase to 6,250 tons occurred.

5. *Jamaica* (1904 output, 1,650 tons).—Beans: Irregular, flat; medium size. Shell: Thick, moist to the touch; dirty. Kernel: Soft; of poor flavour. Jamaica cacaos, with those from St. Lucia, St. Croix, St. Thomas, and Dominica, constitute the lower grades, being usually blended with better quality cacaos for chocolate making. In 1906 Jamaica had increased its output of cacaos to 2,464 tons; St. Lucia showed a decrease to 787 tons in 1906 against 800 tons for 1904; Dominica increased its output of 1904, namely 485 tons, to 590 tons in 1906.

African Cacaos.

1. *San Thomé* (1904 output, 20,526 tons).—Beans: Flat, irregular; more convex on one side than the other. Shell: Dark brown; readily detachable. Kernel: Rich brown; pleasant flavour. San Thomé is a serious competitor of America and the West Indies for the first place among cacao-producing countries. In 1904 it succeeded in standing third; in 1905 it reached the premier position;

Photo, S. E. Jacobson.] [Trinidad.

BAGGING CACAO FOR THE LOCAL MARKET, TRINIDAD.

in 1906 it stood second to Brazil by a small margin of 500 tons; in 1909 it stood third, with an output of 27,232 tons against Brazil 33,036 tons, and Ecuador 30,358 tons.

2. *Cameroon* (1904 output, 1,090 tons).—Beans: Similar to San Thomé. Shell: Rich brown, thick; readily detachable. Kernel: Usually dark violet in colour; harsh and coarse to the palate. Cameroon cacaos are usually mixed with other qualities, as it is too rough for individual use. The cacaos from Cameroon and other districts of British West Africa have greatly improved in flavour and aroma, as the rapidly increasing output testifies. De Candolle's prophecy *—"I imagine it (cacao) would succeed on the Guinea and Zanzibar coasts"—has been verified beyond all expectations, for figures which I have at hand show that the output of cacao from San Thomé has increased from 50 tons in 1869 to 5,570 tons in 1895, to 20,526 tons in 1904, to 24,232 tons in 1906, and to 27,232 tons in 1909—a truly rapid progress. African cacaos come also from the districts of the Gold Coast (1904 output, 5,687 tons), the Congo Free State (1906 output, 396 tons), and Fernando Po (1906 output, 1,533 tons); annually increasing outputs are shown for these three regions of West Africa. In 1906 the output of cacao from British West Africa amounted to 9,586 tons, an enormous increase to this amount being shown in 1909, namely 23,661 tons, the fourth largest output for that year of any cacao-producing country. Of the 1909 output some 7,500 lbs. only were imported into the United Kingdom.

Asiatic Cacaos.

1. *Ceylon* (1904 output, 3,254 tons).—Beans: Rich red-ochre colour; oval; slightly flattened. Shell: Clean, thin; readily detached. Kernel: Red-brown to violet; dry; friable; slightly bitter. This description applies to the finer qualities of Ceylon cacaos, the native beans being

* De Candolle, 'Origin of Cultivated Plants,' 1904, 314.

dirtier in colour and less aromatic in flavour. Cacao is said to have been introduced into Ceylon from Trinidad, and consists in the main of the finer Criollo variety. In 1906 the cacao output of Ceylon had fallen to 2,468 tons, a decrease which is attributed to the prevalence of disease.*

2. *Dutch East Indies* (1904 output, 1,140 tons).—Beans: Similar in appearance to Ceylon, though usually more plump. Shell: Bright brown colour; thin; readily detached. Kernel: Bright brown; slightly bitter. The most important cacaos from the Dutch East Indies come from Java, where it was introduced in 1830. The output of cacao from Java amounted to 1,597 tons in 1906. Java cacaos command a high price on the market, and the better qualities are admirably suited for high-class chocolate manufacture.

Other Countries.

In 1906 the total cacao output of other countries, such as Australasia and certain German and French colonies, reached some 10(0 tons, making the world's output up to 146,87 3 tons.

The following descriptions of different varieties of beans made by the author at the commencement of 1909 and compared with the market prices at that time, give some indication of the relation that exists between physical characteristics and their value to the chocolate manufacturer.

Ordinary Jamaica (50*s*.).—Bean: Irregular; damp to the touch; strong vinegar and winey odour. Shell: Damp; not easily detachable; tough; sometimes covered with white efflorescence; 11·1 per cent. of the bean. Kernel: Harsh and bitter; pale violet to red-brown, usually showing white at fracture.

* Sir W. Ward, H.M. Consul at Hamburg, 'The Grocer and Oil Trade Review,' January, 1908.

Native Ceylon (51*s*.).—Bean: Medium; irregular but flat. Shell: Thin; dirty; not easily detached; 10·75 per cent. of the bean. Kernel: Dull red-brown; bitter but pleasant flavour.

San Thomé (55*s*.).—Bean: Small; dry; clean; shiny; flat. Shell: Cinnamon-brown; thin; dry; showing veins; easily detachable; 11·07 per cent. of bean. Kernel: Violet-brown; pleasant aromatic chocolate flavour; dry and brittle. A good, cheap bean.

Good middling Costa Rica (56*s*.).—Bean: Clean; hard; dry; shiny; flat on one side. Shell: Dry; thin; easily detachable after the bean is broken; 10·5 per cent. of the bean. Kernel: Friable; slightly bitter and astringent; devoid of pronounced flavour.

Superior Bahia (57*s*.).—Bean: Small; irregular; showing veins. Shell: Varying considerably in cleanliness; dry; thin; readily detachable; 11·3 per cent. of the bean. Kernel: Red-brown; uninteresting; bitter.

Middling red Trinidad (62*s*.).—Bean: Irregular; hard; clean; flat. Shell: Red-brown; thin; tough; not readily detached; 12·5 per cent. of bean. Kernel: Tough; rich violet or violet-brown; pleasant cacao flavour.

Fine Guayaquil Ariba (72*s*.).—Bean: Irregular; rough; flat; dry pulp often adhering and causing beans to stick together. Shell: Red-brown to nearly black; dry; not easily detached; 11·2 per cent. of bean. Kernel: Rich dark brown; fine scented flavour; dry and friable.

Finest Trinidad (70*s*.).—Bean: Medium; irregular; slightly flattened. Shell: Thin; dry; showing veins; not easily detached; 15·9 per cent. of bean. Kernel: Brown to violet; fine cacao flavour; slightly bitter.

Good Plantation Ceylon (77*s*.).—Bean: Plump; olive-shaped. Shell: Thicker than Native Ceylon; brick-red; very clean; dry; easily detached; 7·4 per cent. of bean.

Kernel: Dark brown; fine pleasant aromatic cacao flavour; soft and fatty.

TABLE IV.—*Cacao Crops in Tons.*

	1904.	1906.*	1909.†
Brazil	23,160	24,739	33,036
San Thomé	20,526	24,232	27,232
Ecuador	28,433	23,856	30,358
San Domingo	13,557	14,387	14,286
Trinidad	18,574	12,956	22,768
Venezuela	13,048	12,662	16,968
British W. Africa	6,777	9,586	23,661
Grenada	6,226	4,978	6,250
Ceylon	3,254	2,468	—
Jamaica	1,650	2,464	—
Cuba	3,266	2,437	—
Haiti	2,531	2,075	—
Java	1,140	1,597	—
Fernando Po	—	1,533	—
Surinam	854	1,457	—
German Colonies	—	1,347	—
French Colonies	1,215	1,242	—
St. Lucia	800	787	—
Dominica	485	590	—
Congo Free State	231	396	—
Other countries	825	984	—
	146,552*	146,873	174,559

There are many other factors apart from the existing characteristics of the raw commercial bean which regulate the market value, and which are determined by the value of the bean, when roasted, to the chocolate and cocoa manufacturer.

* Sir W. Ward, H.M. Consul General at Hamburg, 'The Grocer and Oil Trade Review,' January, 1908, 1904 estimate 145,913 tons; 1905 estimate 140,976 tons.

† 'Tea and Coffee Journal,' May, 1910.

PLATE XII.

Photo, S. E. Jacobson.] [Trinidad.

BAGGING CACAO BEANS FOR SHIPMENT, TRINIDAD.

Thus, the development of the aromatic oils which takes place during the roasting of cacao, just as during the roasting of coffee, is of the greatest importance to the manufacturer who considers the flavour of his cocoa and chocolate, and is consequently to be taken into account when a variety of bean is purchased.

The percentage of moisture and fat, both of great economic importance to the manufacturer, cannot be accurately gauged by consideration of the external qualifications of the bean alone or without the aid of the chemist. It is proposed, therefore, in the next chapter, to give the chemical composition of the commercial bean in general and of the varieties in particular, collected from the works of Ridenour, Harrison, Zipperer, Dekker, Booth, Ewell, and others.

CHAPTER VIII

COMPOSITION OF CACAO BEANS

Cacao beans, in common with other seeds, contain all the substances necessary to nourish the growing plant during germination, and apart from water the component parts may be divided up under the headings "organic" and "inorganic" constituents.

The organic bodies may, in turn, be divided as follows:

(1) Carbohydrates—such as starch, cellulose, lignin, saccharose or cane-sugar, glucose.

(2) Oils and fats—consisting in the main of olein, palmitin, stearin, and their mixtures.

(3) Pectose group—pectose, pectin, and pectic acid.

(4) Vegetable acids—such as tartaric and acetic acids.

(5) Albuminoids or proteids — such as vegetable albumen.

(6) Amides—diffusible nitrogenous bodies, such as asparagin.

(7) Extractives—such as chlorophyll, tannin, and the alkaloids.

The inorganic constituents consist of salts of various metals, which occur in plant life mainly as—

Inorganic acids	Phosphates Nitrates Silicates Sulphates Chlorides Carbonates	of	Potassium Sodium Calcium Magnesium Iron Manganese Aluminium.
Organic acids	Oxalates Malates Tartrates Acetates Citrates		

TABLE V.—*Analyses of Raw Beans of "Calabacillo" Variety grown in Trinidad.*

	Beans, cuticles and pulp.			Cuticles.		Kernel.		
	Fresh.	Dried.	Fermented and cured.	Dried.	Fermented and cured.	Fresh.	Dried.	Fermented and cured.
Water	61·780	5·000	7·169	12·400	12·400	37·637	5·000	6·080
Albuminoids . .	3·904	9·704	7·213	6·092	6·750	6·696	10·202	7·310
Indeterminate nitrogenous matter . .	0·274	0·681	3·509	Traces	4·006	0·531	0·809	3·106
Theobromine . .	0·814	2·023	1·549	1·599	1·023	1·352	2·059	1·659
Caffeine . . .	0·075	0·186	0·103	0·272	0·355	0·108	0·164	0·058
Fat	15·361	38·181	40·744	2·946	4·000	29·256	44·574	48·400
Glucose . . .	0·862	2·143	0·909	4·811	0·476	0·991	1·510	1·000
Sucrose . . .	0·032	0·079	0·024	0·240	0·143	traces	traces	*Nil*
Starch . . .	2·406	5·980	5·249	6·271	4·865	3·764	5·735	5·329
Astringent matter .	2·776	9·900	5·306	2·621	2·113	5·004	7·624	5·972
Pectin, etc. . .	0·733	1·822	2·671	5·408	6·140	0·657	1·586	1·950
Cacao red . . .	1·772	4·404	2·420	3·391	3·000	2·952	4·497	2·300
Digestible fibre, etc. .	4·847	12·048	11·615	36·388	35·721	5·112	7·287	6·182
Woody fibre . .	2·219	5·515	5·503	8·932	9·840	3·030	4·617	4·600
Tartaric acid (free) .	0·253	0·629	0·535	2·913	0·420	0·079	0·120	0·560
Acetic acid (free) .	*Nil*	*Nil*	0·869	*Nil*	0·720	*Nil*	*Nil*	0·900
Tartaric acid (combined)	0·392	0·974	1·114	2·010	3·450	0·477	0·726	0·624
Iron peroxide . .	0·018	0·044	0·105	0·026	0·057	0·032	0·048	0·115
Magnesia . . .	0·225	0·559	0·686	0·756	0·999	0·324	0·493	0·621
Lime	0·054	0·134	0·207	0·358	0·266	0·054	0·082	0·196
Potash	0·528	1·312	1·125	1·260	1·821	0·142	1·283	0·980
Soda	0·143	0·355	0·120	0·272	0·219	0·239	0·364	0·477
Silica	0·009	0·022	0·065	0·013	0·200	0·016	0·024	0·037
Sulphuric anhydride	0·194	0·482	0·057	0·139	0·085	0·079	0·120	0·051
Phosphoric anhydride	0·442	1·098	1·113	0·763	0·912	0·749	1·141	1·179
Chlorine . . .	0·012	0·014	0·020	0·119	0·019	0·019	0·028	0·021
	100·132	100·319	100·000	100·000	100·000	100·000	100·000	100·000
Total nitrogen . .	—	1·542	2·134	1·542	2·134	1·603	2·472	2·240

In cacao beans the most important organic and inorganic compounds occurring are water, starch, fat, glucose, albumen, theobromine, cacao-red, cellulose or fibre, a small quantity of cane-sugar, and mineral or ash, which consists of silicates, phosphates, sulphates, chlorides, and carbonates of potassium, sodium, calcium, magnesium, iron, and aluminium.

The foregoing table, which the author has arranged from a collection of strictly comparable analyses made by Professor Harrison, throws more light on the composition of cacao beans than any number of words.

This remarkable set of analyses was conducted with the intention of ascertaining the changes taking place in the cacao bean during fermentation, but in the general way it is quite unnecessary to carry out any such elaborate analysis.

The following analyses of raw commercial cacaos, after removal of husk, by Eastes and Terry,* are more typical of general requirements:

TABLE VI.—*Analyses of Kernels of Raw Cacao.*

Kind of cacao.	Moisture.	Fat.	Theobromine	Ash.	H_3PO_4
Caracas	4·75	53·65	1·08	2·76	1·36
Carupano	5·04	47·38	0·87	3·69	1·39
Grenada	5·59	47·12	1·42	2·81	0·91
Guayaquil	3·68	52·97	1·74	3·28	0·85
Para	4·39	57·07	1·00	3·09	1·30
Surinam	2·55	53·70	1·42	2·44	0·85
Trinidad (Common) . .	5·62	45·71	1·05	2·79	0·89
Trinidad (St. Antonio) .	4·72	53·57	1·94	2·70	1·15

A very large number of analyses of commercial cacaos have been made by Ridenour,† a few of which are given below and represent the composition of the husked bean:

* Eastes and Terry, 'Pharm. Journ.,' (3) xv, 764.

† Ridenour, 'Amer. Journ. Pharm.,' 1895, lxvii, 202, etc.

TABLE VII.—*Analyses of Kernels of Raw Cacao.*

	Bahia.	Surinam.	Java.	Grenada.	Guayaquil Ariba.	Surinam (Maracaibo).	Caracas.	Trinidad
Fat . . .	42·10	41·03	45·50	44·11	43·31	42·20	36·81	43·66
Theobromine .	1·08	0·93	1·16	0·75	0·86	1·03	1·13	0·85
Albumen . .	7·50	10·54	9·25	9·76	10·14	11·56	10·59	11·90
Glucose . .	1·07	1·27	1·23	1·81	0·42	1·09	2·76	1·38
Sucrose . .	0·51	0·35	0·51	0·55	1·58	1·36	1·56	0·32
Starch . .	7·53	3·61	5·17	6·27	6·37	1·69	3·81	4·98
Lignin . .	7·86	3·90	6·10	5·55	4·62	7·16	3·28	5·65
Cellulose . .	13·80	16·24	13·85	13·49	14·07	17·32	16·35	13·01
Extractives by difference	8·99	13·53	8·90	9·72	9·00	6·79	12·72	8·31
Moisture . .	5·96	5·55	5·12	5·28	5·90	5·67	6·63	6·34
Ash . . .	3·60	3·05	3·31	2·71	8·73	4·13	4·36	3·60

Filsinger, in the 'Chemiker Zeitung,' in 1887, pointed out that these figures of Ridenour could not be taken as representing normal beans, but with the exception of the low percentage of starch in the beans from Surinam there are no important differences in the figures from those obtained by other observers.

The next table shows analyses of the husked bean, made by various investigators, at widely differing times :

TABLE VIII.—*Analyses of Kernels of Raw Cacao.*

	Guayaquil.			Caracas.		Trinidad.				Surinam.	
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
Water	5·60	3·68	6·33	4·75	6·50	6·20	5·62	6·67	5·23	7·07	2·55
Albumen	14·39	—	11·56	—	16·84	15·36	—	14·38	13·26	21·11	—
Theobromine . . .	1·20	1·74	0·33	1·08	0·77	0·40	1·05	—	0·84	0·50	1·42
Fat	45·49	52·97	52·68	53·65	50·31	51·57	45·71	54·60	50·44	50·86	53·70
Starch	14·30	—	8·29	—	7·65	11·07	—	—	4·20	6·41	—
Woody fibre (cellulose, etc.)	5·80	—	2·89	—	3·0	3·07	—	2·45	6·40	3·02	—
Ash	3·50	3·28	4·11	2·76	4·17	2·87	2·79	2·87	2·75	2·72	2·44

I. Mitscherlich, 'Der Kakao und die Schokolade,' 1859, 57.
II, IV, VII, XI. Eastes and Terry, 'Pharm. Journ.,' 1885, xv, 764.
III, V, VI, X. Zipperer, 'Untersuch. über Cacao, etc.,' 56, 57.
VIII. N. P. Booth, 'The Analyst,' 1909, xxxiv, 137
IX. Bell, 'Thorpes Dict. App. Chem.,' 1905.

Any variations which may be observed in the figures of analyses made by different individuals may be attributed to the varying quality of the cacaos examined, which, as has been previously pointed out, is largely dependent upon the conditions under which it has grown, and the processes to which the beans have been subjected.

As will be seen from the figures given, the principal components of cacao bean are the fat, albuminoids, starch, woody fibre, water, ash, and theobromine, which together constitute about 85 per cent. of the husked bean.

Of these, the fat and theobromine are of the greatest economic value, as the former provides the cacao butter of commerce, which, besides being used for chocolate making, has certain applications in pharmacy, while to the latter is due the stimulating properties of cocoa and chocolate.

Cacao-red and the aromatic oils are of far greater importance than their quantities present in cacao beans would suggest, and though it is not usual to estimate them by analysis, the manufacturer is fully alive to their existence and importance.

Colour and aroma of the resulting cacao preparations are points which must be studied if high-class productions are to be made, and though the attainment of both qualities is mainly in the hands of the planter, the manufacturer can work wonders by careful manipulation in roasting and other processes of manufacture.

It is not intended to give here details of the various components which go to make up the cacao bean, these being reserved for the third part of the book, which deals essentially with the analysis and chemistry of cacao.

The results of analyses of the kernel of raw cacao have been shown, and there remains to be considered the composition of the husks or shells, which should not be employed in the preparation of cocoa and chocolate,

and which should constitute a by-product of the cacao industry.

The husks and shells do not find any application of commercial value until after the beans have been roasted, when they may be employed as cattle food, for the preparation of brown colouring or flavouring matters, for extraction of the 3 or 4 per cent. fat, or even when crystallised in sugar as a sweetmeat.

In the table of analyses by Harrison given at the commencement of the chapter will be found the composition of the husks of the same variety of bean, dried, and fermented and cured. Other analyses show the following to be the components of raw husks.

TABLE IX.—*Analyses of Husks of Raw Cacao.*

	Caracas.		Trinidad.		Puerto Cabello.	
	I.	II.	I.	II.	I.	II.
Moisture	7·74	11·90	8·30	13·09	6·40	12·04
Fat	5·99	4·15	4·23	4·74	4·38	4·00
Albuminoids	11·68	13·95	15·14	13·21	13·75	—
Woody fibre	12·79	17·99	18·00	18·04	14·83	15·98
Ash	8·32	16·73	7·06	7·78	6·06	8·99

With the exception of the percentages of fat in the kernel, and of husk in the whole bean, the analysis of cacao previous to its roasting is of comparatively little importance and of only academic interest. After roasting, however, the more physical properties of the nibs, such as the aroma, their capacity for readily mixing with a large amount of sugar, which is largely dependent upon its percentage of fat, the ease with which the husk is separated from the nib, and the percentage of loss entailed by this process, depending on the proportion of both husk and moisture in the original bean, are of considerable moment to the manufacturer.

Table X.—*Analyses of Husks of Raw Unnamed Cacao, or Mean Analyses.*

	I.	II.	III.	IV.
Moisture . . .	7·83	12·51	—	12·40
Fat	6·38	4·23	3·60	4·00
Albuminoids . . .	14·29	13·58	12·80	10·76
Woody fibre . . .	14·69	16·71	—	9·84
Ash	7·12	10·20	5·70	4·58
Theobromine . . .	—	0·33	0·39	1·02

I. Laube and Aldendorff in König's 'Die mensch. Nahr. u. Genussm.,' i, 261.
II. Zipperer, 'Untersuch. über Cacao, etc.'
III. Dekker, 'Chem. Centr.,' 1902, ii, 1217.
IV. Harrison in Hart's 'Cacao,' 95.

PART II

MANUFACTURE OF CHOCOLATES AND COCOA POWDERS

CHAPTER IX

CLEANING AND SORTING CACAO PRIOR TO ROASTING

The cacao beans of commerce appear on the market in sacks, and, according to the care with which they have been tended during the processes of fermenting and curing, are in a more or less fit state for immediate roasting.

As a rule, however, there is found admixed with the beans pieces of refuse matter—sticks, wood, stones, and pieces of sacking, etc.—which necessitate at least a simple sorting for their removal, and except in the cases of the finest grades, the beans are of such various sizes that it is absolutely essential that some system of separation be employed.

For the best grades of cacao it is the aim of the planter to obtain a uniform size in the beans, but, with all his care, a certain quantity of undersized and shrivelled beans find their way into his sample, and these, if roasted for the same length of time as the bulk, would get over-burnt, and so spoil the quality of the resulting chocolate.

It is not often necessary to wash the beans, though this treatment is employed by some manufacturers with poor and dirty samples.

The same advantages as would be attained by washing would be gained by the treatment of the beans with antiseptic solutions of boracic acid, if the cacao is to be stored for any length of time, or with improving solutions of caustic potash or soda.*

* *Vide* Chapter XII.

Another practice not uncommon with manufacturers is to submit the beans to a "post" fermentation process, by soaking the beans in water for forty-eight hours, and drying off at 45° C., an operation which, in the case of unfermented beans with grey and unattractive shells and a violet bitter interior, is said to greatly improve both the appearance of the bean and the colour and flavour of the kernel.

Whenever washing or treatment with aqueous solutions has been employed, it is necessary to dry the beans as quickly and evenly as possible, in order to prevent the growth of mildew.

If the beans are to be stored for any length of time before roasting, it is advisable to make a careful examination of them on their arrival into the factory, as they may have become damp during transport, in which case the formation of mildew will rapidly bring about deterioration of their flavour, or they may be infected with the eggs of the moth so common in cacao storehouses, and which develop into maggots in early spring, causing considerable damage to the beans.

If the beans are damp they should be spread out on the open floor of a well-ventilated and warm room, though if they are to be treated with water or aqueous solutions as already mentioned, the drying may be postponed till after treatment.

Cacao that has become infected with moth or maggot should be picked over by hand, and the worm-eaten beans removed, while it is a good plan to expose the rest of the beans to the disinfecting rays of the sun, if possible.

All beans are liable to be attacked by the moth, which lays its eggs inside the outer shell of the bean, and even the finest grades of cacao are not immune. The maggots as they hatch out feed upon the contents of the bean, and when sufficiently developed crawl through the

sacking, and swarm over the ceiling and walls of the storehouse.

If the maggots are not destroyed they develop in the summer months into moths, which in their life cycle deposit their eggs in the beans, if such are stored loose, or on the surface of the bags containing the cacao.

The moths may be got rid of by placing large shallow pans of water near and around a lamp in the storehouse, to which they are attracted, and becoming stupefied by the glare fall into the water and are drowned.

In cases where the eggs have been deposited on the sacking, the maggots are less easy to destroy in time to prevent them from attacking the beans, as the newly-hatched larvæ seem to make their way through the sacking to the beans, and when more developed, and after the damage has been done, crawl out and swarm over the room. At this stage they can be attracted to the water in the pans used for destroying the moths, and large quantities can be drowned in this way.

A systematic sorting of the beans and bags before storing is undoubtedly the best remedy against the depredations of moth and maggot, while good ventilation and frequent lime-washing of the walls of the storehouse will greatly aid in keeping these pests in check.

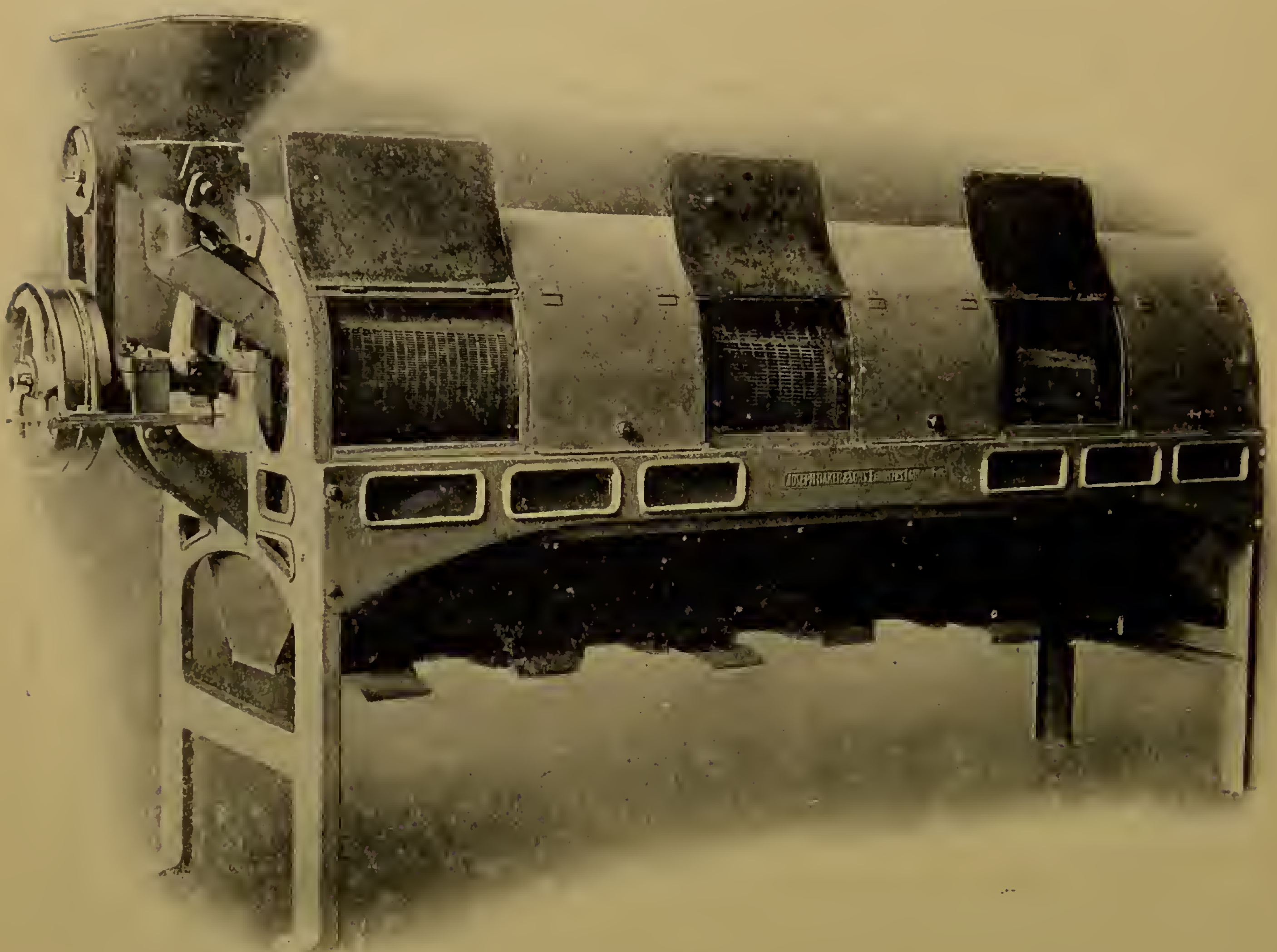
Further information regarding the cacao moth, its life-history and methods for destruction can be found in the records of the Association of German Chocolate Manufacturers.*

Sorting.

In the most primitive form of sorting, and where only small quantities of cacao are to be handled, manual labour is employed, but in large factories it is obvious that such a process would be most costly.

* G. Reinhardt, 'Korr. Verb. Deutsch. Schokoladefab.,' 1891, vii.

Consequently the makers of plant for the manufacture of cocoa and chocolate have turned their ingenuity into devising machinery by means of which a large bulk of beans can be sorted and cleaned. The principle underlying all sorting machines is the progress of the beans through



By permission of Messrs. J. Baker & Sons, Ltd., Willesden.

FIG. 1.—Cacao bean sorting and cleaning machine. (See p. 75.)

a series of sieves of varying meshes, which are usually provided with a rocking motion in order that full advantage of their surface may be taken.

The top and first sieve is of a fine mesh, which will allow only very small and shrivelled beans, small pieces of wood, stone and dust, to pass through. The beans, in

falling to the next sieve, may be winnowed by a power-driven fan in such a way and direction that hollow beans, pieces of sacking, straw, etc., which are lighter than the smallest desirable bean, are blown into a receptacle leading to the passage where the first sievings are descending to the waste outlet.

According to the number of grades required, which are usually two or three, the beans must pass over a number of sieves of different meshes, each sieving being led to a separate outlet. Subsequently the grades may be picked over by hand to remove any defective beans or foreign material that may have escaped the sieving.

It may occur that it is only necessary to pass the beans over the first mesh, if the sample is fairly even in size, in which case they are run from the sieve on to a travelling band, where they are rapidly freed from shrivelled beans and foreign refuse by operators standing in front of the beans as they are carried by.

The machine illustrated (Fig. 1), made by Messrs. Baker and Sons, is constructed so that the beans are fed from a hopper into an inclined revolving cylindrical sieve, divided into six divisions of different meshes. The rough beans in passing over the first division are rid of dirt, dust and small foreign matter, while the remaining divisions grade the beans into various sizes.

It is obvious that a certain amount of foreign matter of similar size to the corresponding grades will be found in the different receptacles among the beans, and to obviate this difficulty a band of canvas can be arranged to take the beans falling from one or two of the different divisions to be picked over by hand. Such a machine, occupying a floor space of $12\frac{1}{4} \times 10\frac{1}{2}$ ft. and 7 ft. high, fitted with a sorting band and capable of large output, would cost about £70.

CHAPTER X

ROASTING OF CACAO—ANALYSES OF BEANS, NIBS AND SHELLS, BEFORE AND AFTER ROASTING

After the process of sorting, the beans are next submitted to roasting, an operation of great delicacy and far-reaching effects.

In the earliest days in the history of chocolate, the Mexicans used to roast their cacao in earthenware vessels over an open fire, and, as in the case of the Chinese cooks of the Philippine Islands of the present day, they succeeded in reducing their appliances for the manufacture of chocolate to a portable form.

A vessel for roasting the beans, and a pestle and mortar for pounding the roasted nibs comprise all the apparatus necessary for the preparation of chocolate, and in spite of the great advances made in the machinery for the manufacture of cacao preparations on the large scale, the principles underlying the modern machines are the same as those of the primitive apparatus employed by the Chinese cook.

The advantages to be derived from roasting are :

(1) Development of the aroma of the beans, which is brought about by changes occurring in the volatile oils at a high temperature.

(2) Change in the colouring matters of the bean.

(3) Gelatinisation of, or rendering soluble, the starch granules.

(4) Modification of the tannin and other astringent matters.

(5) Drying of the husk and bean, so that the former can be readily removed and the latter is freed from moisture, the presence of which would hinder the complete mixing of the fatty nibs when crushed, and tend to destroy the keeping qualities of the cocoa and chocolate prepared from the damp nibs.

The changes that take place in the composition of the bean during roasting are shown in the following table of analyses:

TABLE XI.—*Analyses of Nibs of Cacao Bean, Before and After Roasting.*

	Ariba.		Guayaquil Machala.		Caracas.		Trinidad.		Trinidad.		Caracas.	
	Before.	After.	Before.	After.	Before.	After.	Before.	After.	Before.	After.	Before.	After.
Moisture . .	8·35	8·52	6·33	6·25	6·50	7·48	6·20	7·85	6·34	2·63	6·63	5·69
Fat	50·39	50·07	52·68	52·09	50·31	49·24	51·57	48·14	43·66	41·89	36·81	37·63
Albumen . .	19·40	16·84	12·05	15·58	17·23	19·62	15·80	19·22	11·90	12·02	10·59	12·36
Theobromine	0·35	0·30	0·33	0·31	0·77	0·50	0·40	0·42	0·85	0·93	1·13	0·99
Starch . .	5·78	9·10	8·29	11·59	7·65	9·85	11·07	8·72	4·98	5·70	3·81	6·07
Cellulose or woody fibre	2·70	2·59	2·40	2·59	2·61	2·54	2·63	3·84	13 01	19·64	16·35	11·69
Ash . . .	4·12	3·89	4·11	3·75	4·17	3·92	2·87	4·12	3·60	3·70	4·36	5·03

The first four of these analyses are by Zipperer, made in 1886; the last two are selected from Ridenour's work on cacao and chocolate in the 'American Journal of Pharmacy,' in 1895.

It is somewhat difficult to reconcile the results obtained by these two investigators, for the values obtained for albumen, starch, cellulose, and theobromine are widely different.

It is possible, however, that some of the proteid matter or albumen, as estimated by Ridenour, may be included in his values for extractives, and it is noticeable, also, that the

sum of that observer's figures for starch, cane-sugar and glucose more nearly approaches to Zipperer's figures for starch.

Cane-sugar, glucose and extractives have not been included in the above table, though Ridenour estimated their content in the bean, and they may be found in the 'American Journal of Pharmacy,' vol. lxvii, p. 202.

The important changes which occur during roasting are not very apparent from analyses of beans made before and after the process, though a slight diminution in the percentage of fat and theobromine, and an increase in albumen and starch, are to be noticed.

The form which analysis of nibs usually takes in modern work is illustrated in the next table,* in which it will be noticed that the alkalinity of the ash and percentage of fibre figure prominently.

TABLE XII.—*Analyses of Nibs of Roasted Cacao.*

	African	Grenada	Guayaquil.	Trinidad.	Caracas.	Bahia.	Ceylon.
Mineral matter, total	2·52	2·60	3·16	2·73	3·24	2·68	3·81
Mineral matter, soluble	0·98	1·04	1·32	0 95	1·58	1·22	1·66
Siliceous matter	0·05	0·03	0·04	0·08	0·08	0·05	0·03
Alkalinity of mineral matter as K_2O	0·38	0·55	0·53	0·44	0·74	0·51	0·67
Cold water extract	11·80	9·80	11·40	12·00	—	9·50	11·90
Nitrogen	1·84	2·26	—	2·32	—	1·98	2·44
Fat	50·20	50·80	—	55·70	—	44·40	50·20
Fibre	—	2·94	—	2·48	—	—	2·36

The reason for the inclusion of figures showing the alkalinity of the ash and the percentage of fibre is to detect addition of materials which should be foreign to pure cocoa and chocolate, the former providing information as to whether the cacao has been treated with alkali for making the so-called "soluble cocoa," which will be described more fully in a later chapter, the latter to

* N. P. Booth, 'The Analyst,' 1909, xxxiv, 143.

detect the percentage of husk which has been allowed to remain in the roasted nibs and which should be kept at the lowest possible figure in the manufacture of good cocoa and chocolate.

Analyses of the shells, by the same author, show the following results:

TABLE XIII.—*Analyses of Shells of Roasted Cacao.*

	African.	Guayaquil.	Ceylon.
Mineral matter, total	5·63	8·19	6·61
Mineral matter, soluble . . .	3·53	5·25	4·78
Siliceous matter	1·79	1·45	1·00
Alkalinity of mineral matter as K_2O .	2·63	3·36	2·54
Cold water extract	20·40	24·60	20·70
Nitrogen	2·91	2·13	2·40
Fat	3·50	5·90	3·10
Fibre	12·80	12·85	12·80

Boussingault, in his book, 'Le Cacao et le Chocolat,' gives, among others, analyses of cacaos, before and after roasting, which will be found in Table XIV.

From these results it would appear that a very considerable increase in the percentage of fat occurs on roasting, which cannot entirely be accounted for by the loss of water which takes place at the same time.

The following figures, obtained by the author, show the increase of fat occurring on roasting cacao:

Before roasting certain nibs yielded 40·05 per cent. fat.

After roasting thirty minutes at 145° C., the same nibs yielded 42·76 per cent. fat.

After roasting ten minutes at 145° C., dropping to 110° C., the same nibs yielded 47·84 per cent. fat.

In the case of roasting at 145° C. for thirty minutes, the temperature dropped to 110° C. on admission of the charge of beans, but quickly recovered to 145° C., the resulting roast being distinctly burnt.

Table XIV.—*Analyses of Nibs, without Shell and Germ, Before and After Roasting.*

	Puerto Cabello.		Martinique.		Guayra.	
	Before.	After.	Before	After.	Before.	After.
Water	7·00	5·00	7·50	2·00	7·00	4·60
Fat	40·36	45·23	41·20	45·56	35·96	49·26
Ash	3·75	3·05	2·75	2·90	4·00	3·70
Nitrogen	2·18	2·19	2·25	2·32	2·18	2·20
Albumen	13·60	13·70	14·50	18·00	13·60	14·40

The percentage of theobromine is also affected by the temperature of roasting, thus:

Before roasting certain nibs yielded 1·11 per cent. theobromine.

After roasting at 120° C. for fifteen minutes the same nibs yielded 0·77 per cent. theobromine.

After roasting at 230° C. for eight minutes the same nibs yielded 0·25 per cent. theobromine.

Method of Roasting.

The roasting of cacao is conducted in an apparatus and manner similar to those employed in roasting coffee, though the temperature is not allowed to rise so high as in the latter case.

A good temperature for bringing about the desired chemical and physical changes in the beans is from 125° to 140° C., and the process should be continued till the beans have lost their vinegar-like smell and have developed the aroma characteristic of chocolate.

To determine the degree to which cacao should be roasted is a matter largely of experience, but when the beans have gained a certain crispness, so that the outer shell is easily removed and the aroma has developed, the operation should be stopped and the beans quickly removed

from the roaster and rapidly cooled to prevent "auto" roasting.

Roasting may be conducted over an open fire, by steam, by hot air or by gas.

The first process is the most primitive, and where small quantities of beans are handled is probably the most effective, if careful attention is given to the constant stirring that is necessary to prevent local overheating. If some system of automatic stirring can be arranged, so much the better.

Roasting by steam under pressure is carried out successfully by some firms, though it is improbable that the quality of finest Cacaos can be developed to the best advantage by this method.

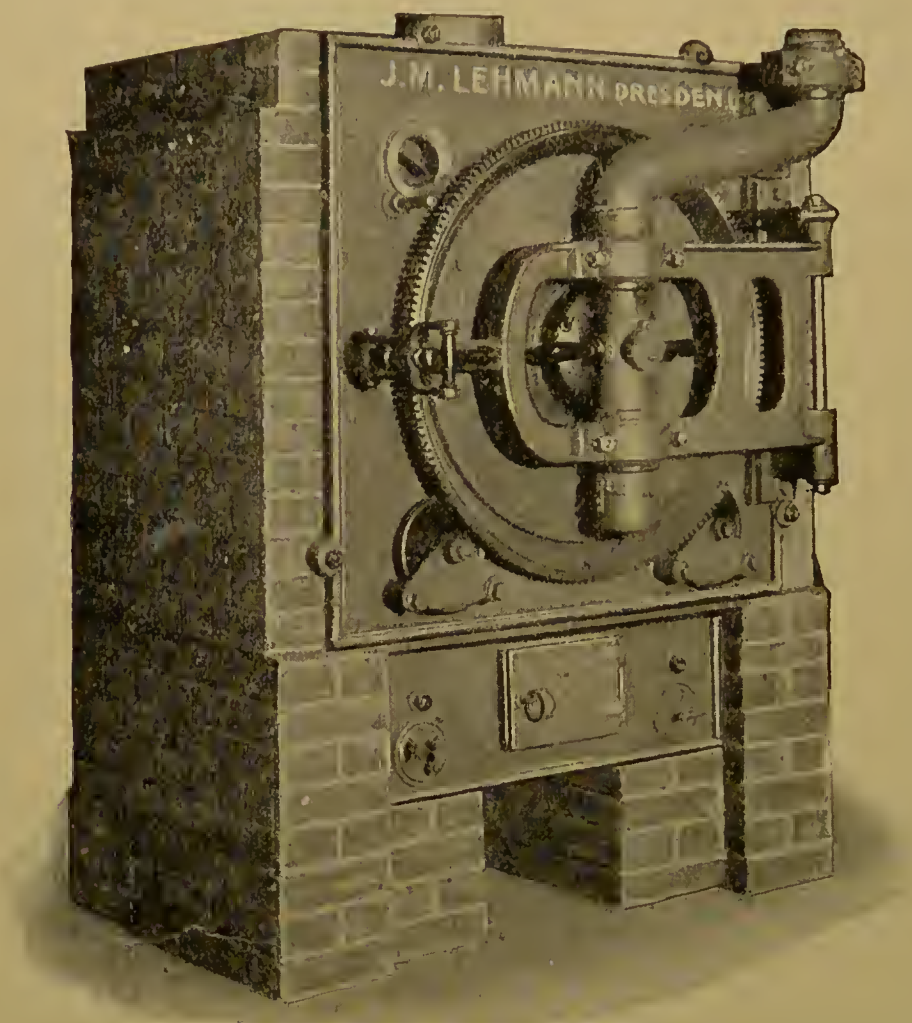
On a large scale the most satisfactory results are undoubtedly obtained by roasting by hot air or gas, and there are many machines now on the market which accomplish the operation in a handy, cleanly and expeditious manner.

Roasting Machines.

In France the most favoured roaster is the "Sirocco," which consists essentially of one spherical receptacle revolving in another, between which pass the hot flue gases from a coke stove removed from the roaster itself. The hot gases are forced to circulate by means of a forced draught. The beans are introduced into a hopper at the top of the roaster, and when the inner receptacle is in position the beans are let down into it, the flues opened and the sphere revolved.

In order to ascertain the progress of the roasting, a sampler is fitted into the axle, which, being hollow at this point, and open on one side to the inner chamber, enables beans to be withdrawn at various stages in the operation.

Beneath the roaster is fitted a large circular open metal trough, in which can be made to revolve a series of fans or brushes that quickly cool the beans let down into it after the roasting is complete. The bottom of the trough is usually perforated and attached to an exhaust fan, which draws cool air through the hot beans.



By permission of Messrs. Bramigk & Co, London.

FIG. 2.—Cacao bean roaster for open fire. (See p. 83.)

Other systems of dry roasting are based on the same principles, though frequently the flue gases are allowed access to the beans direct, a course which, whilst capable of giving very excellent results, can only be recommended where constant supervision is given during the operation, as the beans roast more quickly and are consequently in greater danger of being over-roasted. Where such a

system is in use, the greatest care should be taken that the coke fire supplying the hot gases is quite bright and clear and free from any smoke which might taint the beans.

A machine made by Messrs. Lehmann, of Dresden (Fig. 2), has been designed for giving very quick roasts, and consists of a drum revolving over an open fire, while the process is materially assisted by the passage through the drum of a hot air current, entirely unconnected with the fire gases. By reason of the hot air displacing the vapours coming off the beans, and forcing them through the ventilation pipe in front of the drum, the roasting is considerably accelerated.

This machine is charged through a hopper at the back and is made to discharge automatically, while the drum is designed to revolve while charging, an advantage which prevents the over-roasting of the beans that first come in contact with the hot metal.

The sampler, is placed in a similar position to that of the "Sirocco" roaster, namely, in the drum axle.

An ingenious system of rapid roasting of ordinary and medium grades of hard-shelled beans is one embodied in a roaster made by Messrs. Baker and Sons, of Willesden. In this design the beans are fed through the end of a cylinder and continually fall, until roasted, through hot gases supplied by burning an admixture of town or "Producer" gas and sufficient air to ensure complete combustion.

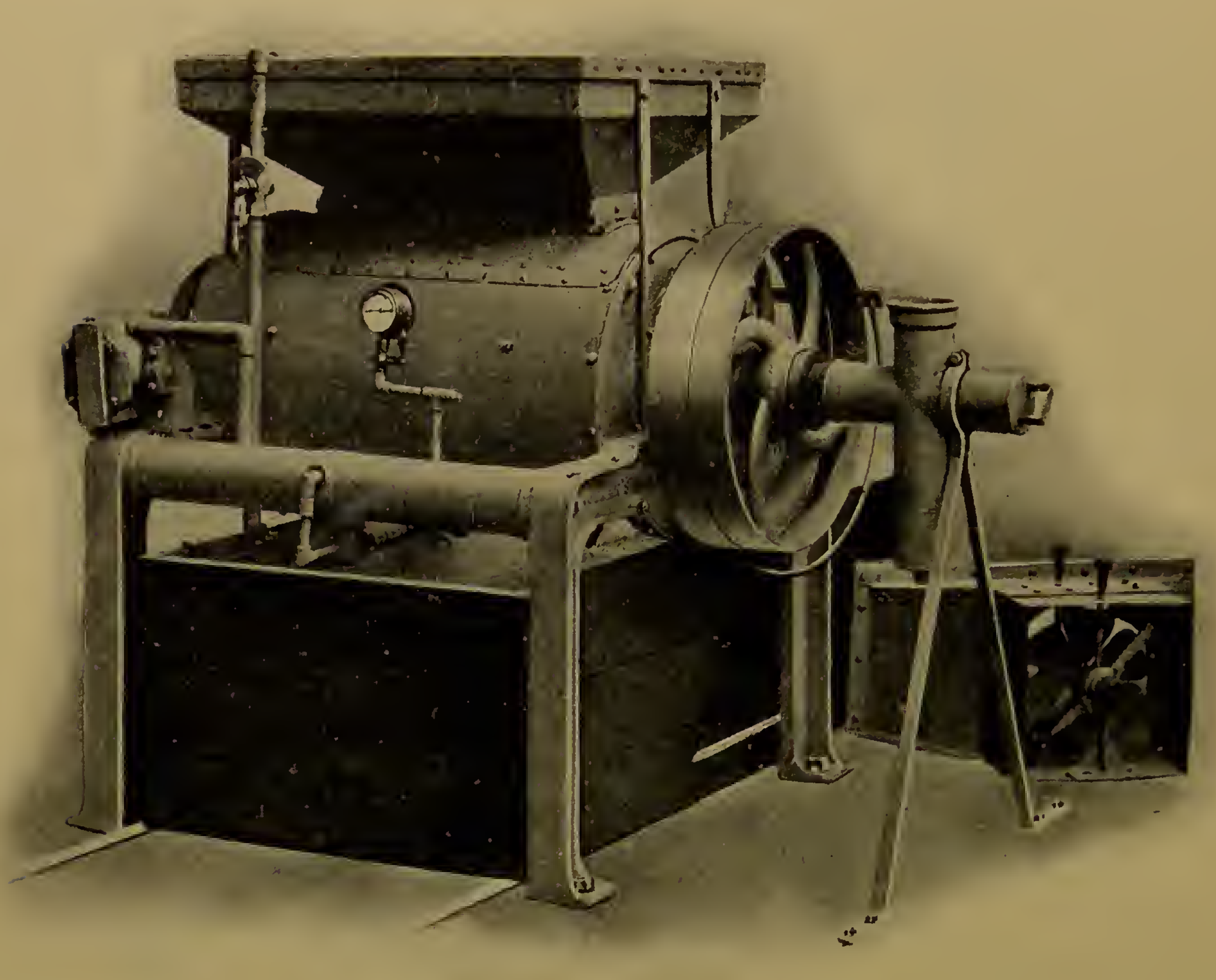
Movable coolers with perforated bottoms can be supplied with this roaster, and after receiving their charge they can be wheeled away to an exhaust fan for cooling.

The whole machine is simple, strong, and capable of a large output, as the process of roasting is much shorter than in the externally heated machines which are next described.

Like the "Sirocco," the externally heated roasters

consist of one drum or cylinder revolving in another. The heat is supplied to the outside of the inner drum or cylinder by a series of gas burners, and an exhaust pipe carries off the steam and fumes from the roasting beans.

Exhaust coolers can be fitted to these machines, so



By permission of Messrs. J. Baker & Sons, Ltd., Willesden.

FIG. 3.—Cacao bean roaster for gas. Externally heated. (See p. 85.)

that when the cacao is ready to be discharged the cooler is run underneath and the beans are allowed to fall into it. It is then run out on rails to the fan, which draws cold air through the hot beans into the space beneath the false and perforated bottom with which the coolers are provided, and thence through the fan to the outside of the building.

Such a machine adapted for town or "Producer" gas heating, fitted with a cooler, and of a capacity of 200 lb. per roast, would occupy a floor space of 7½ ft. by 6 ft., and can be obtained from Messrs. Baker and Sons for £80 (Fig. 3).

The cacao roasting machine built over an open fire, and with a hot-air current passing through the drum, as already described, can be obtained from Messrs. Bramigk & Co., who are the sole agents for Messrs. Lehmann's machinery in this country. With a similar capacity to the externally heated roaster, the machine would occupy a floor space of about 6 ft. by 4½ ft., and would cost £59 10*s*. 0*d*.

The roasting process is the most important in the course of manufacture, and special care should be bestowed upon it, as no correction can afterwards be made if a bad roast has been produced.

An easy access to the interior of the roasting drum for purposes of thorough cleansing is essential, as adhering shells of previously roasted beans are bound to occur, and becoming burned in subsequent roasts will affect the aroma of the resulting cocoa.

Especially is this the case with beans previously treated with alkaline solutions.

CHAPTER XI

NIBBING, HUSKING, AND WINNOWING THE ROASTED CACAO—ANALYSES OF NIBS AND SHELLS, AND THEIR PROPORTIONS IN THE ROASTED BEAN

The cacao beans, after having been roasted and rapidly cooled down on one of the exhaust coolers already described, are taken when slightly warm to be husked or deprived of their shell.

This process briefly consists of cracking the beans between two set rollers, and the broken pieces are made to pass over a series of sieves of different mesh, while an air draught, travelling in an opposite direction to the nibs, blows the husk from them.

The beans should not be allowed to get stone cold before passing through the rollers, as the kernel is liable to be broken up into very minute pieces, and particles of the same weight as the shell may be blown away into the husk receptacle, causing considerable loss.

The quality of cocoa and chocolate is largely dependent upon the completeness of this process, for it must be realised that the nibs of cacao beans alone should be used for cacao preparations, and that the inclusion of husk must be looked upon as adulteration.

With modern machinery there can be no excuse for the presence of husk in a cocoa or chocolate, and by a careful adjustment of the fans the complete separation of nib and husk can be effected.

So important has the detection of added or included husk to cocoa become that there is no scientific journal dealing with analysis of food stuffs and prevention of fraud and adulteration without its article on the subject.

The problem of estimating the percentage of husk in cacao preparations has always been of great consequence, and Filsinger, one of the earliest investigators on cacao and its preparations, describes a method of calculating the shell content by a deposition method in glycerine and water, an operation which from its primitive and unscientific nature is incapable of giving reasonably consistent results.

The determination of the quantity of cellulose present in the cacao preparation is a good indication to what extent the original nibs have been cleaned or adulterated, as the greater the proportion of husk the higher will be the value for cellulose.

TABLE XV.—*Estimations of Cellulose in Cleaned Roasted Nibs.*

	Cellulose.	
	For 100 parts cacao.	For 100 parts cacao insoluble in water.
Sancheize	4·90	14·75
Bahia	4·76	14·64
Haiti	4·86	14·60
St. Lucia	4·50	13·80
Guadeloupe	5·03	15·15
Trinidad	5·00	15·27
Grenada	4·93	15·05
Maragnan	4·66	14·51
Carupano	5·11	15·61
Porto Plata	4·63	14·14
Caracas (small)	5·53	16·60
Mean	4·90	14·91

The above table shows very recent results for the estimation of the percentage of cellulose present in pure cacao paste or ground cleaned nibs, given by Dr. Bordas,

Director of the Laboratories of the Ministry of Finance in France, at the Seventh International Congress of Applied Chemistry, held in London in 1909.

The estimation of cellulose alone, however, may be misleading, as extraordinary fluctuations occur in the quality of beans, so that under normal conditions one bean may contain more tissue than another in the kernel itself, thus showing a higher cellulose content.

More precise and accurate figures may be obtained by estimation of the quantity of ash, its acidity value and composition, and especially of the amount of silicic anhydride, of which the husk contains a much larger quantity than the kernel.

The composition of the ash obtained from various cacaos is given by Dr. Bordas as follows:

TABLE XVI.—*Composition of Ash.*

	Ash.		SiO_2 and sand.	Cl.	SO_3.	Fe_2O_3 Al_2O_3.	CaO.	MgO.	P_2O_5.	K_2O.	Na_2O.	CO_2 by difference.
	Sol.	Insol.										
Bahia . .	33·33	66·66	1·30	0·20	2·57	0·60	3·60	15·65	32·60	37·96	1·50	3·72
Haiti . .	30·26	69·74	7·34	0·48	2·66	1·93	5·18	14·15	27·65	30·41	2·63	7·57
St. Lucia .	31·25	68·75	0·93	0·30	3·00	0·99	5·25	15·21	33·78	38·50	1·50	5·54
Guadeloupe .	33·14	68·86	4·18	0·50	3·06	1·33	5·00	14·14	29·22	34·94	1·27	6·36
Trinidad .	32·55	67·45	7·00	0·40	3·80	0·74	3·54	15·43	28·38	32·28	1·90	5·53
Grenada .	31·03	68·97	1·50	0·35	3·51	0·25	3·82	17·62	32·94	33·96	0·26	5·79
Maragnan .	27·36	72·64	0·60	0·30	4·00	0·58	4·46	17·74	31·28	38·00	0·16	2·88
Carupano .	33·76	66·24	3·50	0·20	3·35	0·36	3·66	16·06	30·10	32·91	0·60	9·16
Porto Plata .	32·10	67·90	0·53	0·25	3·10	0·65	3·40	16·00	33·50	38·30	1·50	2·77
Caracas (small)	34·12	65·88	7·00	0·20	3·10	1·82	4·30	13·00	25·60	32·50	2·50	7·98
Germ . .	56·67	43·33	1·00	0·50	4·24	0·40	4·30	9·73	18·50	54·50	0·50	4·93
Shell (roasted)	43·15	56·85	19·10	0·80	2·50	3·60	4·72	7·40	8·50	4·50	3·50	9·38
Dust and small cacao . .	35·56	64·44	26·52	—	—	—	—	—	—	—	—	—

A very accurate method for detection of added husk to cacao by estimation of the pentosans, fully described in a later chapter, is given by R. Adan.* The committee

* R. Adan, 'Internat. Cong. App. Chem.,' 1909, viii, c. 194.

regulating the Bromatology Section at the 1909 International Congress of Applied Chemistry suggested that the following resolution should be submitted:

"The Congress, believing that the determination of pentose and pentosans affords an excellent criterion of the purity of cocoa powder, recommends the adoption of this determination in the routine analysis of cocoa."

Adan's results are embodied in Table XVII.

TABLE XVII.—*Analyses of Shelled Cocoa Nibs.*

	Moisture.	Fat.	Starch.	Ash.	Cellulose.	Pentosans.			
						Grains.		Shells.	
						Initial substance.	Powder with 30 per cent. fat.	Dry substance.	Substance with 10 per cent. moisture.
Ariba . .	8·27	45·15	5·83	3·88	4·48	1·71	2·79	—	—
" roasted	8·52	50·07	9·10	3·89	3·70	1 29	2·19	—	—
" shells	—	—	—	—	—	—	—	9·97	9·11
Port au Prince	7·77	46·35	5·97	4·15	5·19	1·59	2·60	—	—
" roasted	4·73	51·87	8·40	3·49	4·31	1·27	1·99	—	—
" shells .	—	—	—	—	—	—	—	7·57	6·92
San Thomé .	8·08	46·61	5·69	4·28	4·43	1·43	2·34	—	—
" roasted	5·71	50·20	13·27	3·89	4·33	1·45	2·57	—	—
" shells .	—	—	—	—	—	—	—	8·49	7 92
Caracas . .	7 77	45·54	5·48	4 91	6·18	1·56	2·71	—	—
" roasted	7·48	49·24	9·85	3·92	4·24	1·19	1·86	—	—
" shells .	—	—	—	—	—	—	—	7·78	7·11
Bahia . .	5·96	42·10	7·53	3·63	7·86	2·19	3·14	—	—
" roasted	3·71	50·19	9·61	3·24	3 93	1·77	2·73	—	—
" shells .	—	—	—	—	—	—	—	9·45	8·70
Soconusco .	2 95	43·38	8·33	3·21	3·34	1·59	2 60	—	—
" roasted	5·00	50·22	9·58	3·76	3·78	1·21	2·06	—	—
" shells .	—	—	—	—	—	—	—	10·53	9·51
AVERAGE . .	6·43	44·44	8·22	4·00	4·78	1·53	2·47	9·96	8·21

From these figures it will be seen that the inclusion of

husk in cacao preparations, whether deliberate or accidental, can be readily detected by the chemist.

The Association of German Chocolate Manufacturers offered a prize some years ago for a machine that would separate the nibs completely from the husk without allowing any quantity of the former to find their way into the waste receptacle.

The problem was not so easy of solution as would be imagined, for the bean, when passing through the crushing rollers, is certain to break up into a number of different-sized particles, the smaller of which, being light, could not help passing along with the husk, or being sieved out with the dust and finer particles of the shell.

Stimulated by this offer, many machines claiming to do the required work were quickly put on the market, and though a large number succumbed when put to the test, several were taken up by the larger manufacturers.

Method of Nibbing, Husking, and Winnowing.

In all machines employed for nibbing, husking, and winnowing, the first step is to reduce the beans into small fragments.

This is brought about by passing the cacao through two rollers which are so adjusted to the size of the roasted beans that they do not crush too severely but crack the outer crisp shell, and enable the nibs or portions of the kernel into which it is divided to fall away.

The fragments fall into an inclined revolving cylindrical screen, divided into meshes of various sizes; the first division removes the dust and very small particles of cacao, while the remaining divisions grade the nibs according to their size. A current of air capable of being regulated so as to effect the separation of husk from particles of the nibs, which may be of the same size as, but specifically

lighter than, the shell, is supplied to each division by means of a separate fan.

The cylindrical sieve may contain any number of meshes of different sizes, so that nibs of any desired grade can be obtained. In the larger machines there may be six or eight divisions, though the more usual number is three or four.

Nibbing, Husking, and Winnowing Machines.

In one machine, made by Messrs. Baker and Sons (Figs. 4 and 5), the beans are passed through two rollers, capable of being set to any required dimension to suit the size of the sample or for purposes of regulating the grade of the nibs. The crushed beans are carried to the top of the machine by an elevator, and are discharged into an inclined cylindrical sieve. Separation of the husk from the nibs is efficiently carried out by fans with independent air inlets, and which can be separately controlled. The machine is made with six or eight divisions, and the cylinder has a corresponding number of different meshes, while two of the sections are fitted with narrow longitudinal openings through which the germs pass, excluding the greater part of the cacao, which passes over into later divisions.

Complete separation of the germ from the finer cacao is carried out in the germ separator, which is described later as an independent machine.

The heavier pieces of shell to which some cacao has remained adhering, and the pieces which have not passed through any division of the sieve, fall at the end of the machine into a worm conveyor, and are returned to be passed again through the rollers.

In the ordinary winnowing machines, the germ, which is the dead embryo or radicle of the seed, is not separated

from the nibs at this stage, but being of a hard, gritty and fibrous nature, and of coarse flavour, it must be removed

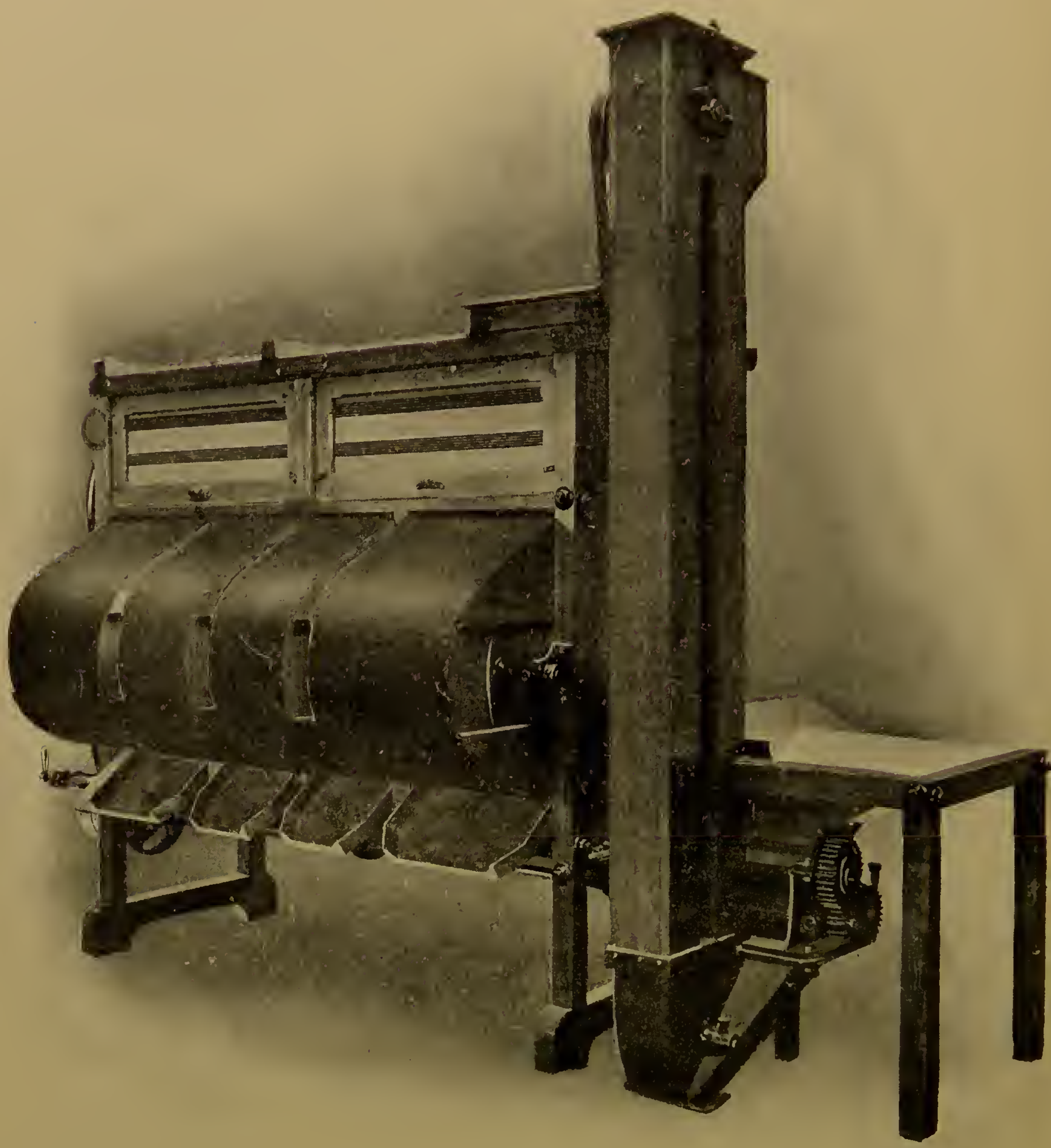


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Fig. 4.—Cacao nibbing, husking and winnowing machine. Front view. (See p. 91.)

before converting the nibs into cocoa powder or chocolate.

Germ Separating Machine.

The separation is usually effected in a cylinder, either

By permission of Messrs. J. Baker & Sons, Ltd., Willesden.
Fig. 5.—Cacao nibbing, husking and winnowing machine. Back view. (See p. 91.)

perforated with longitudinal slits, through which the germ and small cacao pass, which can again be separated by a

system of winnowing, or indented in such a manner that the cavities are capable of taking the small fragments of cacao, but will not hold the elongated germ.

The cacao grains in the cavities pass upward beyond a light scraper until they reach a certain elevation, when a brush removes them from their holes and they fall into a trough, where a worm conveyor carries them away. The germ, on the other hand, not fitting into the cavities, remains below the scraper, and by the tilt of the cylinder is made to pass in an opposite direction to the cacao, complete separation being thus effected.

The nibbing, husking and winnowing machine already described, and fitted with a germ separator, costs about £120 to £140, and will occupy approximately 12¾ ft. by 7¾ ft. floor space, and is about 9 ft. high.

The following figures given by Hart * as the result of some experiments on the loss, etc., during manufacture are interesting. Only small samples were dealt with, however, and the percentage loss is consequently higher than it would be on the manufacturing scale.

TABLE XVIII.—*Losses in Preliminary Preparation of the Beans for Manufacture.*

	Fine clayed Venezuela.	Fine Trinidad.	Ordinary Trinidad.
Before roasting	100	100	100
Weight of husk	16·8	16·3	15·3
Loss (apart from husk)	7·7	5·1	6·7
Weight of dry cacao after removal of fat	55·0	56·0	54·8
Weight of fat extracted	12·3	16·4	16·1
Loss during grinding and expression of fat	8·2	6·2	7·1
Total loss on manufacture (including husk)	32·7	27·6	29·1

The figures have been calculated on 100 parts of bean,

* G. H. Hart, 'Cacao,' 1900, 113.

and have been adjusted to suit the requirements of manufacturers.

Filsinger,* from a sample of 100 lb. of Machala cacao containing equal parts of large and small beans, obtained the following divisions: 70 parts large nibs, 9·2 parts medium nibs, 0·8 parts radicles or germ, 10 parts husk, 4 parts cacao waste, 6 parts loss.

The four parts of cacao waste on further sifting yielded about 30 per cent. each of nib, husk and cacao dust, the remainder being waste and loss.

The great improvements which are said to have taken place both in the quality and yield of the beans and in the machinery for preparing them for chocolate manufacture are not very apparent from the following figures, showing the losses sustained during preparation, made by Bernhardt† in 1889.

TABLE XIX.—*Losses in Preliminary Preparation of the Beans for Manufacture.*

	Mean.	Maximum.	Minimum.
Sifting	2 80 per cent.	5·49 per cent.	1·10 per cent.
Picking	0·80 ,,	2·09 ,,	0·25 ,,
Roasting	5·51 ,,	7·05 ,,	4·61 ,,
Cleaning	13·00 ,,	16·04 ,,	10·08 ,,
Total loss	22·11 ,,	25·78 ,,	16·76 ,,

* Filsinger. 'Zeitsch. offent. Chem.,' 1898, 810.

† Bernhardt, 'Chem. Zeit.,' 1889, 32.

CHAPTER XII

MILLING—PREPARATION OF COCOA POWDER—EXPRESSION OF CACAO BUTTER—"SOLUBLE" COCOA POWDERS

WHETHER for chocolate or cocoa making, the nibs freed from their husks and germs are subjected to a milling or grinding process.

In the first case, this is necessary so that an even and smooth chocolate may result, and the nibs be reduced to an easily handled form.

In the latter case, it is necessary to obtain the cacao in as highly a pulverised state as possible previous to the extraction of fat, so that after the fat or cacao butter has been expressed the mass may be removed, rapidly pounded and sieved.

THE CACAO MILL.

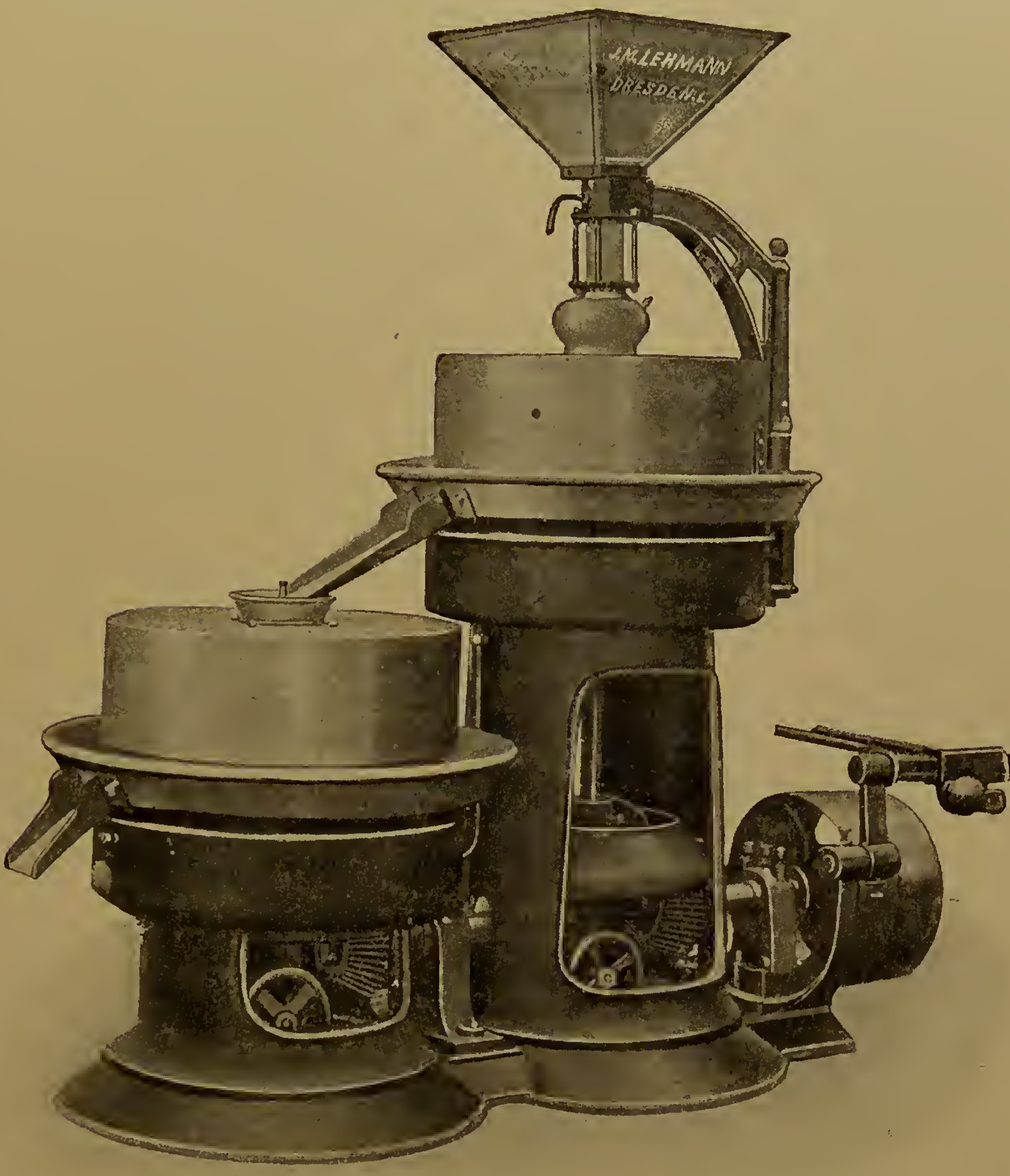
In modern mills the nibs are fed into a hopper, so as to fall between a pair of revolving stones, which are the highest and first of a series through which the paste will have to run.

As the nibs contain a large percentage of fat they are readily reduced to the liquid state by the application of heat, and to this end the stones under which they pass are usually encased in steam-heated jackets.

The grinding mill may consist of a single, double, or

triple pair of stones, the liquid cacao running from one to the other in succession, to undergo further reduction.

The cacao mass flowing from the last pair of stones is



By permission of Messrs. Bramigk & Co., London.
FIG. 6.—Twin cacao mill. (See p. 98.)

in a semi-liquid state, at a temperature of about 45° C., and is run into deep pans, where it is allowed to solidify. The blocks of raw or bitter cacao are stored in a cool place, ready either to be used as the base for chocolate, or for

re-melting, preparatory to being placed in the hydraulic presses for expression of the fat. Single, double, triple or even five-stoned mills can be obtained from any maker of chocolate machinery, and though their introduction is of comparatively recent origin, they are now looked upon as necessary additions to the cocoa and chocolate factory.

The reduction of the nibs to a fine homogeneous mass facilitates the incorporation of the sugar, which is added to it in the "melangeur" if chocolate is to be manufactured, and enables blends of different varieties of cacao beans, separately roasted, to be made so that a uniform and even mixture is obtained.

In the double cacao mill illustrated (Fig. 6), the capacity of output is about 1,000 lb. of the finest cacao liquor per ten-hour day. It occupies about 8 ft. by 3 ft. floor space, and is 7 ft high. The cost of such a machine is £130.

It has been proved that stones of too large a diameter often overheat the cacao and damage the flavour of the product, and in the machine designed by Messrs. Lehmann this danger has been obviated by very careful consideration given to the size limit, without curtailing the output. Only a slight warming of the stones by means of the steam coils underneath is required before starting.

The feeding apparatus is adjustable and acts automatically, while the rate of progress of the nibs through the mill can be watched through a glass tube connecting the hopper to the first pair of stones, and controlled at any time without difficulty.

Preparation of Cocoa Powder and Expression of Fat.

It has already been shown that cacao nibs contain some 50 per cent. of fat. This high content of fat makes the consumption of the beverage prepared from pure cacao

too rich and indigestible for persons afflicted with weakness of the stomach, and moreover the presence of so large a quantity of fatty matter prevents the complete mixing of the cocoa and water used in its preparation.

In the early days of cocoa powders the fat was extracted by submitting the nibs to a lengthy boiling in water, when the fat rising to the surface was skimmed off and purified, and the nibs, partially defatted, were placed in linen bags and subjected to a pressure at a temperature about the boiling-point of water to remove further portions of fat and moisture. In this way about 50 per cent. of the fat present was removed, but the resulting cocoa powder was of poor quality, having lost its fine aroma and colour from prolonged boiling in water, and was, moreover, liable to turn mouldy owing to the presence of moisture which it still contained.

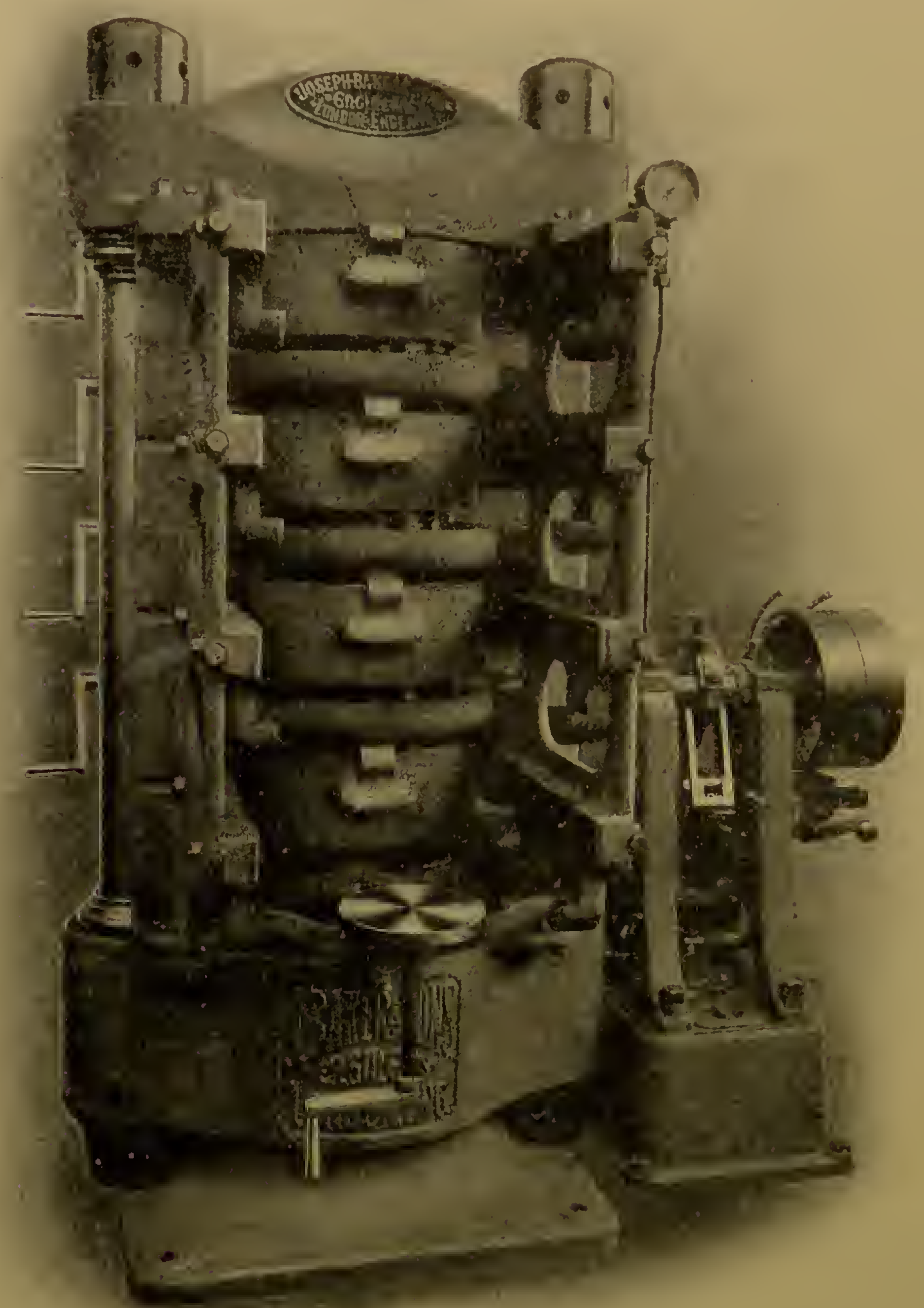
Other methods still in existence of lowering the percentage of fat in cocoa powder are by means of additions of starch and sugar. Such preparations cannot be termed "cocoa powder," which should consist of pure defatted cacao, but rather "chocolate powder," and when sold to the public should bear a printed notification of any added material.

The Cacao Butter Press.

The method now usually adopted in the preparation of cocoa powders is to run the cacao mass from the grinding mills direct into a press, where it undergoes extreme pressure applied hydraulically, whereby some 60 to 70 per cent. of the fat is removed.

In the modern cup hydraulic cacao press, of which an illustration is given (Fig. 7), the framework receivers and plunger dishes are of cast iron and are made with steam passages, so that the machine can be rapidly heated ready

for use. The receivers slide forward on rails for filling, and the capacity of a four-pot machine is about 90 lb. per charge of four receivers. If a smaller charge is required to



By permission of Messrs. J. Baker & Sons, Ltd., London.
FIG. 7.—Hydraulic cacao butter press. (See p. 99.)

be expressed, any of the receivers may be fitted with iron dummies so that one or all the pots may be temporarily put out of use.

When the press is working a piston fits telescopically into each cup, and the pressure, provided by a pump, forces the fat from the nibs, while the close fitting of one part in the other and the inclusion of filter-pads prevent the escape of the cacao mass with the fat.

In the machine illustrated, made by Messrs. Baker & Sons, the press has been built for a working pressure of 100 atmospheres, and the over all dimensions are 4 ft. 7 in. long by 3 ft. 8 in. wide by 5 ft. 10 in. high.

Such a machine costs £185, the price including the pump and one set of filter-pads.

The fat extracted by this method will require filtering if it is to be put upon the market, though such a course will be unnecessary if used direct in the factory.

If purification of the fat is necessary it may be melted down and allowed to settle in a warm room and the top portion drawn off when all the sedimentary matter has settled to the bottom, or it may be filtered through a series of flannel bags.

For filtering large quantities special machinery has been designed, in which the molten fat is passed first through a hair sieve to remove larger particles of cacao, etc., and is then run into hanging removable filter-bags kept warm in a large tank, which receives the filtrate, and which is fitted with a gauze glass so that the level of the fat in the tank can be ascertained.

Where large quantities of nibs are to be expressed a battery of presses may be employed with advantage, and considerable economy and time can be effected by using an accumulator attached to one large powerful pump. The pressure is maintained in the accumulator, which is connected to the pump on the one hand and with the presses on the other.

The accumulator is coupled up with the presses through suitable inlet valves, and each press being furnished with a

pressure gauge and the necessary valves, and the actions of the pump and accumulator being automatic, the work is greatly simplified and a constant pressure maintained.

The fat or "cocoa butter" of commerce should be pale yellow and of a pleasant chocolate aroma and flavour. If too great heat has been used during its expression the fat will be a dull greyish white, while if the beans have been insufficiently roasted the smell and taste of the butter will be "green" and unpleasant.

As in all cases of manufacture, technical skill and experience produce the best results, and even with the highly efficient machinery at the command of the manufacturer, bad and inferior cocoas and cacao butters are placed on the market through little or no attention being paid to the details of one or other of the many processes through which the cacao has to pass before being fit for consumption.

Cocoa Crushing Mill and Disintegrator.

The cocoa left in the press, after the fat has been expressed, is removed and allowed to cool. It is then passed through a crushing mill, which consists of a pair of rollers fitted with teeth, and the mass is reduced to a fine powder.

It may then be passed through another pair of smooth rollers, which completely disintegrate the powder, and, after slight beating to reduce the cocoa to a light friable state, it is conveyed to the sifting machine.

Cocoa Sifter.

The sifter consists of a hopper into which the powder is delivered, and which, being furnished with a shake feed, delivers the cocoa into a rotating inclined hexagonal drum covered with fine mesh silk.

The sifted cocoa falls into draws, and the tailings and

matters which do not pass through the fine mesh are carried over into a receptacle placed at the end of the machine, whence it can be conveyed and returned to the crushing or disintegrating rollers to be re-ground.

The cost of a pair of crushing rollers will be from £40 to £70, the disintegrator about £60, and the cocoa sifter from £35 to £75, the prices varying with the size and maker. All the machines mentioned may be obtained from Messrs. Baker & Sons, Messrs. Lehmann, and other large manufacturers of cocoa- and chocolate-making machinery.

A complete plant made by Messrs. Lehmann, of Dresden, designed so that the machines may be worked in conjunction with one another by means of worm conveyors and elevators, forms a system for the automatic pulverisation and sifting of cocoa powders under most favourable conditions. The output of the plant is about one ton of cocoa powder per day, and costs £312 10*s*.

"Soluble" Cocoa Powders.

The term "soluble" as applied to treated cocoa powders is undoubtedly a misnomer, for the property attempted to be acquired by the manufacturer of so-called "soluble" cocoa is the formation of an emulsion which is not easily deposited at the bottom of the cup when boiling water is added. At first this result was obtained by the incorporation of starchy matters with the cocoa powder, so that the starch, gelatinising on addition of boiling water, made a sticky and viscous mass, which materially hindered the heavier particles from settling.

Hassall * was a strong opponent to this method of rendering cocoa powder "soluble," and in his book on 'Adulteration of Food, etc.,' condemns the practice not only by showing microscope drawings of pure cocoa powders

* Hassall, 'Food: its Adulteration, etc.,' 1876.

against those of cocoas with the addition of starch, but also by quoting lengthy cross-examinations of witnesses at the Parliamentary Commission held to investigate the matter.

James Bell, in 'The Chemistry of Foods,'* says: "Most of the other preparations of cocoa, whether sold as soluble cocoa or chocolate, consist of mixtures of cocoa nibs with various substances ground together into a smooth paste. In the manufacture of soluble cocoa, arrowroot, sago, or some other starch and sugar, either dry or in the form of a syrup, are combined with the cocoa nib paste. The admixture of starch with the cocoa paste tends to mask the presence of the fat, and to render the cocoa more readily miscible with boiling water."

C. J. Van Houten was the first to attempt to treat cacao with chemicals, so as to render it more readily miscible with water without the addition of foreign starches.

By treating cacao with alkalis, such as potassium or sodium hydrates or carbonates, ammonia or magnesium carbonate, the tissues of the kernel are partially disintegrated, and the material is capable of suspension in water or milk to a greater degree.

The addition of alkalis to cacao has not met with unqualified approval, and there are many who, while readily acknowledging the superiority of the beverage resulting from the beans or cocoa so treated, are not prepared to admit that the inclusion of chemicals is not prejudicial to health.†

However this may be, the so-called "solubility" of modern cocoa powder is a distinct advantage to the consumer, and, in the opinion of many, the treatment which it undergoes greatly enhances the flavour.

Bordas ‡ has discussed the matter at some length, and

* J. Bell, 'The Chemistry of Foods,' 1887, 74.

† *Vide* Discussion in Reports of Congress at Geneva and Paris, 1908, 1909.

‡ Bordas, 'Ann. Falsific,' 1910, iii, 61–70.

admits that though French manufacturers in general do not add alkali salts for the purpose of producing "soluble" cocoa, the importation into France of foreign cocoa so treated has, of late years, reached very large proportions.

In considering the desirability of addition of alkalis from the point of view of health, and the need of regulating by law the quantity added, the same author points out that natural cacao mass contains from 2·46 per cent. to 3·05 per cent. of potash, estimated as K_2O and calculated on the dry fat-free substance, whilst samples of "soluble" cocoas contain from 4·82 per cent. to 6·41 per cent. of the same material. As there is no direct evidence of injury done to the health by the consumption of such cocoas, Bordas concludes that, provided the quantity of potash is not allowed to become excessive, there is no harm in treating the cacao with alkalis.

The same author points out that Belgium, Italy and Switzerland prohibit the sale of cocoa containing more than 3 per cent. of alkaline carbonate, and in Roumania the limit is fixed at 2 per cent. The United States prohibit the sale of cocoa containing any added alkali, and the same regulation obtains in Austria.

Methods of Application of Alkali.

The treatment of the cacao with alkali may be accomplished with water and heat, with or without pressure, with the alkalis potassium, sodium or magnesium carbonates, which are usually used in Holland, or with solutions of ammonia or ammonium carbonate, generally employed in Germany. The hydroxides of sodium and potassium are also used in the production of "soluble" cocoas.

The alkalis may be applied before, at the time of, or after roasting, before the pressing and consequently after milling, or after the pressing.

There is therefore plenty of scope for the manufacturer,

and if one method does not give the required result, another may be tried, for the treatment with any one alkali at any one stage does not produce a cocoa similar in flavour or qualities to that treated at a different stage in its manufacture with a different alkali.

If the cacao is to be treated before roasting the beans may be subjected to the influence of steam and ammonia, which is the method suggested by Staehle in a German patent. In the process he suggests this operation is carried out below 100° C., and the beans are subsequently roasted at 130° C., when the ammonia, being volatile, is driven off and the aroma developed.

Neumann, in a French patent obtained in 1909, washes the beans in a solution of alkali at 50° C. The cacao is removed, and the temperature gradually raised to 120° C., when the beans are roasted. In subsequent processes the shells are removed and the nibs ground to a paste, when, before or after expressing the fat, the mass is again gradually heated to 100° C., and ground in a "melangeur" from one to twenty-four hours. By this means he claims to obtain a "soluble" cocoa powder of fine flavour.

The beans may be treated with alkali after a slight roasting; thus in one process the beans, after being gently heated, shelled and expressed, are sprinkled with a solution of potassium carbonate containing 1·5 per cent. to 3 per cent. of the alkali. If too much alkali has been added, so as to give an unpleasant taste to the cacao mass, a solution of tartaric acid is added to neutralise the effect. The mass is now fully roasted over a gentle fire in a clean roaster, and great care has to be taken to prevent the treated cacao from burning, as the mixture clinging to the revolving roaster is likely to become superheated where in contact with the metal. Subsequently the dried cacao is expressed.

Neumann, in an English patent, 1910, adopts a somewhat similar process. By this method the beans are

completely roasted and husked, and the nibs, reduced to a coarse meal, are slightly pressed to get rid of some of the fat. The partially defatted cacao is then treated with alkalis and again pressed.

In yet another process magnesium carbonate, or, better, a strong solution of caustic potash (90–95 per cent.), is mixed in or sprayed on to the cacao paste from fully roasted beans, and, after thorough incorporation, the treated mass is pressed in the usual way. Another process is described as follows: "To 100 lb. of cacao paste are added 2 to 3 lb. of potash, dissolved in 1 to $1\frac{1}{2}$ gallons of water, and the whole is thoroughly kneaded in a dough mixer or apparatus of similar construction. If ammonium carbonate is used instead of potash, $\frac{1}{2}$ to 3 lb. are used for the same bulk of cacao paste with the same volume of water. The treated cacao is then placed in the hydraulic press and the fat expressed."

The application of alkali may be made after the fat has been expressed in the form of a liquid spray, and in such cases potassium carbonate and not ammonia or ammonium carbonate solutions should be used, as it is extremely difficult to rid the treated cacao of the ammoniacal smell if no high temperature is employed subsequent to their application. In all cases where aqueous solutions are used care should be taken to free the cacao mass or powder from water, as without such precaution the resulting powder is liable to turn mouldy.

There are other processes for making "soluble" cocoa powders which do not entail the use of alkalis, but as these depend largely on treating the cacao with boiling sugar, it has been thought desirable to defer their discussion until a later chapter, which deals with cocoa preparations and mixtures of cocoa with sugar, milk powder, etc.

Owing to the considerable demand for "soluble" cocoas in recent years, it has been found necessary to

increase the efficiency of existing machinery, and to create new, in order to accelerate the process.

Messrs. Bramigk and Co. have given the following estimate for the plant of machinery necessary to manufacture about 1 ton of pure soluble cocoa essence per ten-hour day, and the machines included are chosen as being specially adapted for the purpose :

	£	*s.*	*d.*
1 machine for cleaning and sorting cocoa beans	76	0	0
2 cocoa-roasting machines, as illustrated, @ £59 10*s.*	119	0	0
1 exhaust fan, with two cooling trolleys .	26	5	0
1 cocoa-crushing, cleaning, hulling and separating machine	136	0	0
1 germ-separating machine	34	0	0
3 triplet cocoa mills, similar in working to double mill illustrated @ £166 10*s.* . .	499	10	0
3 hydraulic cocoa butter presses, with one accumulator	562	10	0
1 automatic pulverising plant, consisting of : 1 breaking machine 1 pulveriser 1 sifting machine	312	10	0
	£1765	15	0

Total H.P. required, about 20.

CHAPTER XIII

ANALYSES OF COCOA POWDERS "SOLUBLE," DIETETIC, PROPRIETARY, Etc.

According to the treatment which the beans have undergone described in the preceding chapters, so will they show on analysis varying fat and ash contents, and differing values for the alkalinity of the mineral matter.

Thus, a powder which has been heavily expressed may show as low a fat content as 10 per cent., rising to 40 per cent. if the pressure of the extracting press has been light.

Or, again, the application of fixed alkalis, such as potash and potassium, sodium or magnesium carbonates, will be more apparent in the analyses of the finished cocoa powder if it has been made to the nibs, cacao paste or powder, than in cases where the beans have been treated with their shells on.

The volatile alkalis, ammonia or ammonium carbonate, will not appear on analysis, as it is improbable that they form any stable compounds with the component parts of the cacao. On the other hand, a cocoa powder showing a very high percentage of nitrogen may be suspected of being treated with, and not freed from, ammonia, though it is unlikely that any ammonia or its compounds could be present without serious detriment to the flavour.

Stutzer,* however, who has made a close study of the

* Stutzer, 'Zeitsch. angew. Chem.,' 1891.

effects of the different processes of manufacture on the resulting analyses, claims to be able to detect cocoas prepared by treatment with ammonia. His results are given in Table XX.

TABLE XX.—*Analyses of Cocoa Powders, showing influence of methods of manufacture on the figures obtained.*

	I.	II.	III.	IV.
Water	4·30	3·83	6·56	5·41
Fibre	3·36 }	37·48	39·99	36·06
Nitrogen-free extract	38·62 }			
Total nitrogenous substances[1] . . .	20·84	19·88	20·93	19·25
Fat	27·83	30 51	27·34	33·85
Ash[2]	5·05	8·30	5·18	5·43
	100·00	100·00	100·00	100·00
[1] Containing total nitrogen . . .	3·68	3·30	3·95	3·57
Composed of—				
Theobromine	1·92	1 73	1·78	1·80
Ammonia	0·05	0·03	0·46	0·33
Amido-compounds	1·43	1·25	0·31	1·31
Digestible albumen	10·25	7·68	10 50	7·81
Indigestible nitrogenous substances .	7·18	9·19	7·68	8·00
Containing nitrogen	1·15	1·47	1·23	1·28
Proportion of total nitrogen indigestible	31·2	44·5	31·2	35·8
[2] Containing—Total P_2O_5	1·85	2·52	2 14	2·05
P_2O_5 soluble in water	1·43	0·50	0·74	0·77
Ratio of *total* P_2O_5 to *soluble* . . .	100:77	100:19	100:34	100:37
Ash soluble in water	3·76	4·76	2·82	2·76
Ratio of *total* ash to *soluble* . . .	100:74	100:57	100:54	100:49

I. was composed of forty parts Ariba, forty Machala, and twenty Bahia beans, and was manufactured by Wittekop and Co. without the use of chemicals.

II. was a sample of well-known cocoa manufactured in Holland with the addition of potash.

III. and IV. were German cocoas prepared, according to Stutzer's opinion, by the application of ammonia.

An interesting series of analyses of cocoa powders made by Hughes* at the request of the Planters' Association of Ceylon is given in Table XXI, which, besides showing the percentage chemical composition, indicates the mechanical condition, which is of great importance in both cocoa and chocolate manufacture.

TABLE XXI.—*Analyses of Cocoa Powders.*

	Cadbury's.	Fry's.	Van Houten's.	Rowntree's.	Tibbles'.	Epps's.
Price per lb.	2s. 4d.	2s. 1d.	3s. 0d.	2s. 9d.	2s. 9d.	1s. 2d.
Water (loss at 100° C.)	3·99	4·30	2·94	3·82	5·04	4·58
Fat (cacao butter)	25·01	30·70	30·10	32·50	27·10	26·40
Albuminoids and theobromine	22·15	20·38	21·64	19·30	17·53	7·27
Mucilage, gum, etc.	9·70	10·64	10·03	9·04	11·86	11·82
Sugar, glucose and dextrin	4·10	1·36	0·97	1·76	2·34	18·53
Starch and digestible fibre	25·91	23·76	21·44	21·83	27·10	28·45
Indigestible fibre	4·13	4·46	4·26	3·83	5·33	1·40
Ash or mineral matter	5·06	4·40	8·62	7·92	6·50	1·50
	100·00	100·00	100·00	100·00	100·00	100·00
Melting-point of fat	28·9°C.	29·4°C.	28·9°C.	29·4°C.	26·7°C.	28·3°C.
Containing nitrogen	3·50	3·22	3·42	3·05	1·77	1·55
Containing potash	1·66	1·56	4·49	4·24	2·68	0·54
Mechanical condition:						
Powder passed through sieve (10,000 holes to the square inch)	72·59	81·78	57·05	62·51	76·35	42·74
Residue left on sieve	27·41	18·22	42·95	37·49	23·65	57·26
	100·00	100·00	100·00	100·00	100·00	100·00

In considering these figures the author points out that in Cadbury's and Fry's cocoas about two-thirds of the original fat of the cacao had been removed, but they were otherwise untreated. Van Houten's and Rowntree's cocoas were taken as samples of cocoa powders in which two-thirds of the original fat of the cacao had been removed and which had been treated with potash salts.

* Hughes, 'Analyses of Samples of Cacao,' 1899.

To both Tibbles' and Epps's cocoa powders other materials, such as starch and sugar, had been added, and consequently in these powders the chemical components of cacao were found in reduced proportions.

In the four samples, Cadbury's, Fry's, Van Houten's and Rowntree's, no foreign starch or sugar was present, the amount of reducing matter and starch found being due to that naturally existing in cacao.

Analyses of various commercial cocoa powders are published from time to time, and in Table XXII will be found a few in which the acid equivalent of the ash (the number of c.c.'s of $\frac{N}{10}$ acid required to neutralise the ash from 2 grm. of sample) has been converted into alkalinity expressed as K_2O, in order to conform with that value expressed in the same way by the greater number of observers.

TABLE XXII.—*Analyses of Well-known Brands of Commercial Cocoa Powders.*

Constituents.	Fry's Cocoa Extract.		Van Houten's Cocoa.			Rowntree's Extract of Cocoa.		Blooker's Dutch Cocoa.		Bensdorp's Pure Royal Dutch Cocoa.	Cadbury's Cocoa Essence.
	I.	II.	I.	II.	III.	I.	II.	I.	III.	II.	II.
Moisture	—	4·33	—	4·53	—	—	4·05	—	—	4·59	4·00
Ash { Total	4·24	4·28	8·64	8·19	7·96	8·48	7·70	6·06	6·10	6·69	4·70
Ash { Alkalinity as K_2O	1·33	—	3·68	—	1·81	3·82	—	2·21	1·24	—	—
Fat	30·95	31·16	29·80	29·78	29·66	27·56	30·82	31·48	27·07	33·06	27·58
Extractive soluble in water	—	5·26	—	9·88	—	—	7·48	—	—	8·52	6·48
Theobromine	—	1·36	—	0·69	2·00	—	1·08	—	1·90	0·88	0·70
Starch	—	16·07	—	21·26	—	—	—	—	—	11·33	21·05
Albumen	—	12·78	—	17·03	—	—	15·22	—	—	11·41	13·58
Fibre	3·89	—	4·38	—	—	4·42	—	3·76	—	—	—

I. E. E. Ewell, 'Bull No. 13, U.S. Dept. of Agriculture.'
II. Florence Yaple, 'Chem. Zeit.,' 1895, Rep. 21, 240.
III. C. Girard, 'Internat. Cong. App. Chem.,' 1909, Sect. VIII, C. 185.

In considering the figures for the alkalinity of the ash in the above table, it should be noticed that Girard's values are made on the ash soluble in water only, while Ewell's are on the total ash, and will include the calcium and magnesium carbonates, which would not be found among the soluble portion.

Girard, whose work, already quoted, was primarily undertaken for the purpose of studying the presence of oxalic acid and the estimation of the same, gives some tables showing the analyses of various cocoa powders of commerce, and the composition of their ash. His results are so particularly valuable and enlightening that it has been thought desirable to include them here in full.

TABLE XXIII.—*Analyses of Commercial Cocoa Powders.*

	Van Houten's.	Déjong's.	Fabriqué à Amsterdam.	Bensdorp.	Suchard.	Blooker.	Conté.	Menier.	Moreuil	Chocolaterie Ouvrière.
Ash	7·96	7·22	6·98	6·70	6·36	6·10	6·36	4·84	4·36	4·18
„ insoluble . .	15·57	16·61	19·19	22·38	22·01	25·90	21·06	55·77	58·25	60·28
„ soluble . .	84·43	83·39	80·81	77·62	77·99	74·10	78·94	44·23	41·75	39·72
Alkalinity of soluble ash as K_2O . .	1·81	1·98	1·47	1·27	1·43	1·24	1·38	0·47	0·49	0·40
Sucrose . . .	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*
Reducing matters .	Traces	Traces	Traces	Traces	Traces	Traces	Traces	Traces	Traces	Traces
Fatty matter . .	29·66	30·27	25·07	29·77	31·67	27·07	29·18	23·27	34·64	36·46
Melting-point of fat	31·0°	29 8°	30·4°	31·2°	30·2°	30·8°	30·4°	30·4°	30·6°	30·4°
Jean refractom: value of fat . .	−20	−17·5	−18·5	−19	−19	−19	−19	−18	−18·5	−18·5
Saponification value of fat . . .	192·7	193·6	192·3	193·0	192·8	192·6	193·6	193·0	192·2	192·1
Iodine value of fat .	35·4	39·4	38·0	36·3	37·4	34·9	37·6	37·4	36·7	39·0
Theobromine . .	2·00	1·88	2·06	2·05	1·94	1·90	2·16	2·24	1·84	1·04
Oxalic acid . .	0·406	0·630	0·630	0·567	0·566	0·504	0·630	0·653	0·536	0·504

Leaving for one moment the ash and its values, the significance of the other figures is worthy of brief consideration at this point.

Sucrose.—The absence of sucrose in the powders shows that no addition of sugar has been made, and that the

beans were well fermented (*vide* Chapter VIII, Table V, Sucrose).

Reducing matters.—The presence of only traces of reducing matters shows that the beans have been well fermented, for cacao kernels have been shown to contain 1·5 per cent. of glucose and other reducing matters when merely dried and up to 1·0 per cent. if slightly fermented. If the beans have been thoroughly fermented there should be only traces of reducing matters.

Fatty matter.—The lowest percentage of fat is shown in Menier cocoa, and the highest in "Chocolaterie Ouvrière." The percentage of fat has been shown to depend upon the degree of expression to which the roasted nibs are subjected.

The melting-point, refractometer, saponification and iodine values of the fat fall within the limits of those obtained for pure cacao butter, and consequently in the powders analysed, no addition of, or adulteration with, foreign fat has been made. The interpretations of these values and the methods for their estimation will be discussed fully in the third part of the book.

Theobromine and oxalic acid.—The percentages of both these constituents of cacao are mainly of academic interest, though if the beans had been too highly roasted the quantity of theobromine, to which is due the stimulating nature of cacao preparations, would have been lower than 1·0 per cent of the powder.

In considering the ash percentage and values, it will be desirable to tabulate the chemical composition of the mineral matter or ash obtained from the different cocoa powders. The mineral matter has been completely analysed by Girard, and his results will be found in Table XXIV.

Ash.—In the first seven powders the sum of the potash and soda values equals some 50 per cent. of the total ash,

TABLE XXIV.—*Analyses of Ash obtained from Commercial Cocoa Powders.*

	Van Houten's.	Déjong's.	Fabriqué à Amsterdam.	Bensdorp.	Suchard.	Blooker.	Contó.	Menier.	Moreuil.	Chocolaterie Ouvrière.
Ash soluble in water :										
Potash as K_2O	22·71	52·07	47·68	45·31	42·41	45·15	46·77	22·68	24·23	19·73
Soda as Na_2O	22·32	0·71	1·03	0·61	0·85	0·61	0·86	2·44	0·50	2·40
Sulphuric anhydride SO_3	1·84	1·59	3·20	2·59	2·29	2·00	2·47	2·58	2·60	2·30
Chlorine Cl.	0·96	0·45	0·58	0·45	0·57	0·77	0·19	0·61	0·18	0·67
Phosphoric anhydride P_2O_5	21·54	17·08	17·46	17·40	19·82	18·26	19·23	7·64	6·98	8·30
Carbonic anhydride CO_2	14·39	12·46	10·96	10·84	11·13	9·73	10·00	7·85	6·66	6·60
Lime and magnesia CaO and MgO	Traces	Traces	Traces	Traces	Traces	Traces	Traces	Traces	Traces	Traces
Ash insoluble in water :										
Potash as K_2O	0·26	0·26	Traces	0·54	0·31	0·83	0·93	6·85	10·68	11·04
Soda as Na_2O	—	—	—	—	—	—	—	—	—	—
Lime CaO	1·25	1·93	2·39	3·35	2 26	1·78	3·21	3·39	3·42	3·26
Magnesia MgO	10·33	9·84	11·17	12·09	11·96	11 99	11·67	16·57	15·19	16·32
Iron oxide Fe_2O_3	0·83	0·78	0·61	0 52	0·50	0·98	0·61	0·49	0·50	0·76
Alumina Al_2O_3	0·15	0·31	0·19	0·15	0·18	0·67	0·24	0·08	0·09	0·37
Silica SiO_2	0·77	0·69	1·56	0·49	0·85	1·38	0·53	1·67	1·91	2·06
Phosphoric anhydride P_2O_5	2·59	1·59	3·11	5·31	5·72	6·13	2·38	24·77	20·63	22·36
Carbonic anhydride CO_2	0·28	0·24	0·19	0·45	1·28	0·19	0·95	2·50	6·48	3·98
Sulphuric anhydride SO_3	Traces	Traces	Traces	Traces	Traces	Traces	Traces	Appreciable traces	Appreciable traces	Appreciable traces
	100·22	100·10	100·13	100·10	100·13	100·17	100·04	100·13	100·05	100·15

though only in the first does the quantity of soda amount to any appreciable quantity.

In this case the powder must certainly have been treated with sodium hydroxide or carbonate, since the ash of normal untreated powders contains some 30 per cent. of potash (K_2O), as will be seen in the last three cocoas, which have been prepared without the addition of alkali, and which do not themselves contain more than $2\frac{1}{2}$ per cent. of soda.

In the cocoas 2 to 6 inclusive it is safe to say that either potassium hydroxide or carbonate was used to render them "soluble," and their addition, as also of the soda in the first, has succeeded in fixing the phosphoric, carbonic, and sulphuric acids originally present as insoluble compounds. That is to say, the alkali added has attracted to itself the acid portions of the powders forming soluble salts, with the result that on analysis those cocoas treated with alkali are found to contain soluble ash with greatest proportions of potassium, sodium, or magnesium salts of phosphoric, carbonic, and sulphuric acids, according to which alkali has been used.

In the last three cocoa powders the comparatively low percentage of potash, soda, and phosphoric and carbonic acids in the soluble ash tend to show not only that the cocoas were prepared without the addition of alkali, but also that the remainder of these components not to be found in the soluble ash are combined in some probably complex form, which will not split up without the presence of excess of alkali, and will consequently figure in the ash insoluble in water.

Dietetic, Proprietary, and other Cocoa and Chocolate Powders.

Cocoa powders should contain the roasted, partially defatted kernels of cacao beans only. The chemical

composition of such cocoa powders will depend upon the amount of expression to which the nibs have been subjected. If 30 per cent. of fat has been expressed, which is usually the highest limit, the resulting cocoa powder will show 25–35 per cent. fat, 4–5 per cent. ash, 3–5 per cent. fibre, 12–17 per cent. nitrogenous matter as albumen, 11–20 per cent. starch, and 4–5 per cent. moisture.

"Soluble" cocoa powders treated with alkali should consist of the roasted, partially defatted kernels of cacao beans, with the addition of sodium or potassium hydroxide or carbonate, or magnesium carbonate, and if the nibs have 30 per cent. of fat removed will show on analysis from 25–32 per cent. fat, 6–8·5 per cent. ash, 3–4·5 per cent. fibre, 11–17 per cent. nitrogenous matter as albumen, 11–19·5 per cent. starch, and 4–5 per cent. moisture. If the cocoa powders have been rendered soluble by treatment with ammonia or ammonium carbonate, or by steam, their analyses will be similar in the main to those of untreated cocoas.

Any additions of foreign matters other than alkali must be looked upon as adulteration, unless it is clearly expressed on the wrapper or packet containing the powder that such additions have been made.

Cocoa powder is such an excellent medium for conveying materials possessing special medicinal or food values, being a strongly flavoured and palatable article of food, that it is frequently used as the base for preparations used for dietetic purposes.

If, as has been previously shown, additions of foreign matters, such as starch and sugar, which are cheaper and which consequently might be used for purposes of adulteration, are made, it is most necessary that the consumer should realise that he is buying cocoa powder with such additions, however innocuous or even advantageous to the food value of the preparation their presence may be.

The addition of starch to a cocoa powder serves the double purpose of increasing the carbohydrate content of the preparation and of rendering the powder more digestible for those who are unable to assimilate the more fatty cocoas.

There are on the market many of these nourishing cocoa powders which contain selected arrowroot and other starches, with or without the addition of sugar, and which are certainly improved from the food point of view by such addition.

Epps's cocoa contains 40 per cent. cocoa, 16 per cent. West Indian arrowroot, and 44 per cent. sugar, from evidence given in the case of *Gibson* v. *Leaper*, though Ewell* gives the following analysis: 3·15 per cent. ash (alkalinity as K_2O = 0·6), 25·94 per cent. fat, 1·51 per cent. fibre, 26·0 per cent. sugar, and much arrowroot starch.

Under this heading must certainly be included chocolate powders, which, consisting of powdered chocolate, or cocoa and sugar and starch, give similar analyses to that of Epps's cocoa. There is, however, this difference, that the latter, being a standard proprietary article, is mixed with great care and from carefully selected ingredients, while some of the chocolate powders which have come under the author's notice have not shown much careful selection of ingredients, and have more frequently than not been freely mixed with cocoa shell powder.

Chocolate powders are as a rule very cheap, but there is no reason why they should be nasty, and if good clean starch has been added to powdered chocolate the resulting preparation should be as good and wholesome as the best proprietary articles.

The chocolate powder prepared by the Chocolat Menier Company showed the following analysis, according to Ewell:

* E. E. Ewell, 'Bull. No. 13, U.S. Dept. of Agriculture.'

1·40 per cent. ash (alkalinity as $K_2O = 0·47$), 21·31 per cent. fat, 1·10 per cent. fibre, 58 per cent. sugar, and no added starch.

J. Bell, in his 'Analysis and Adulteration of Foods,' also gives an analysis of a prepared cocoa thus: 4·95 per cent. moisture, 24·94 per cent. fat, 23·03 per cent. sugar, 19·19 per cent. starch, 2·24 per cent. nitrogen; the starch and sugar were both added.

E. J. Clayton * has made analyses of different samples of cocoa essence, which consisted of partially defatted and otherwise treated cacao; a very complete investigation into the component parts of the ash obtained from them was made.

Recommendations have been made from time to time of treating the cocoa powder with boiling sugar, and many patents have been taken out to this end.

Greiser, in an English patent, 1909, suggested that moisture and volatile bodies that affect the flavour should be removed in a uniform manner by heating the finely ground cocoa (with or without the addition of sugar) *in vacuo* at, say, 70° to 90° C. Or the mass might first be boiled *in vacuo*, then melted with a suitable proportion of sugar and again boiled *in vacuo*.

Langen, in a French patent, 1909, proposed to treat the partially defatted cocoa with a boiling solution of sugar in a vessel fitted with a suitable stirrer. The mixture should be stirred until cold, and the mass of chocolate thus obtained powdered and pressed into moulds or mixed with milk powder. By this treatment he claimed to obtain a readily soluble cocoa or chocolate for use as a beverage.

Many more such instances could be cited, though they are only worthy of consideration as showing the extent to which the subject of rendering "soluble" cocoa has been studied. It must be admitted that the majority of the

* E. J. Clayton, 'Chem. News,' 1902, lxxxvi, 31.

patents taken out are not only of little value for making the cocoa "soluble," but the processes employed usually spoil the aroma of the cocoa and are quite impracticable to work outside the laboratory or experimental room.

Foreign matters with medicinal and other special virtues are frequently added to cocoa powders, amongst others being acorn and barley meal, malt, milk powders, dried egg-albumen, saccharin instead of sugar for persons suffering from diabetes, kola seeds, peptone and other such materials.

In a U.S. patent, 1910, Collett and Eckardt have recommended the addition of one or more ferments capable of producing lactic acid from carbohydrates without evolution of gas to cocoa or chocolate.

There can, however, be only a very limited sale for all these kinds of preparations, and as this work deals essentially with cocoa and chocolate, and not with all the possible additions that may be made, further consideration of them has not been considered necessary.

CHAPTER XIV

PREPARATION OF CHOCOLATE—MIXING—REFINING

Unsweetened chocolate should be prepared exclusively from the roasted kernels of the cacao bean, with or without the addition of a small quantity of flavouring matter. The chocolate should contain at least 45 per cent. of cacao butter, the natural fat of the cacao bean.

Unsweetened chocolate, which is seldom met with in confectioners' shops, and is usually sold to manufacturers of special chocolate who do not possess their own roasting, nibbing and milling plant, is prepared from the cacao mass running from the grinding mill previously described in Chapter XII. In fact, the milled, roasted cacao nibs constitute in themselves pure unsweetened chocolate, and consequently on analysis they will show the correct composition for that variety.

The cacao mass flowing from the mill is in liquid form, and according to the degree of grinding to which it has been subjected, will be found to be in a more or less finely divided state. In order to obtain a smooth homogeneous paste it is necessary to pass the cacao mass through a series of granite or steel rollers, which, running at a high speed, reduce the chocolate to the finest possible form.

The rollers or refiners will be described fully later in the chapter, when the refining of sweetened chocolate is dealt with.

Sweetened chocolate should contain the kernels of roasted and shelled cacao bean, with the addition of not

more than 60 per cent. of sugar, with or without a small quantity of flavouring matter.

The base of sweetened chocolate will therefore be pure unsweetened chocolate or the cacao mass running from the mills. To this base is added a sufficiency of sugar and flavouring matter in such a way that a smooth homogeneous product shall result.

Method of Mixing.

The mixing of the sugar and flavouring matters with the cacao mass is conducted in a large revolving pan in which run a pair of granite rollers. The pan revolving horizontally carries the cacao mass under the rollers, which being capable of adjustment up and down, are themselves caused to revolve by the friction of the cacao passing under them.

It is advisable to give the cacao mass some thirty to forty-five minutes working in the mixer or "melangeur" previous to introducing the sugar, as in this way a certain homogeneity is obtained in the base, and the work of the refining machines is somewhat facilitated.

The sugar should be ground fine in a disintegrator or sugar mill, passed through a fine lawn mesh, and thoroughly dried before being mixed in with the cacao mass.

Much time will be saved if the "melanguer" is heated up to a temperature 5° or 6° above the melting-point of the cacao butter, say to 40° C., and to bring about immediate blending of the sugar and cacao mass both ingredients should be heated to about 35° C. before being placed in the "melangeur."

The principle of the "melangeur," which has been briefly described, is to obtain the complete blending of the ingredients, the reduction of the mass to a finer state of division, and the lightening of the paste. The first object is brought about by the revolving pan travelling at fairly high speed, carrying the mass under and round the rollers,

and by a series of scrapers which guide and turn the paste into the required direction. The constant friction of the pan, which travels at a higher speed than the rollers, rubbing on the cacao mass at the two obstructions, raises the temperature of the whole, and gradually reduces the particles to a finer state of division.

After the paste has been passed through the refining rollers the mass is dry and lifeless, and it is necessary to place it again in the "melanguer" to beat some life into it. This is brought about by the constant friction of the chocolate mass on the rollers and the re-melting of the cacao butter, which has dried up in the process of refining.

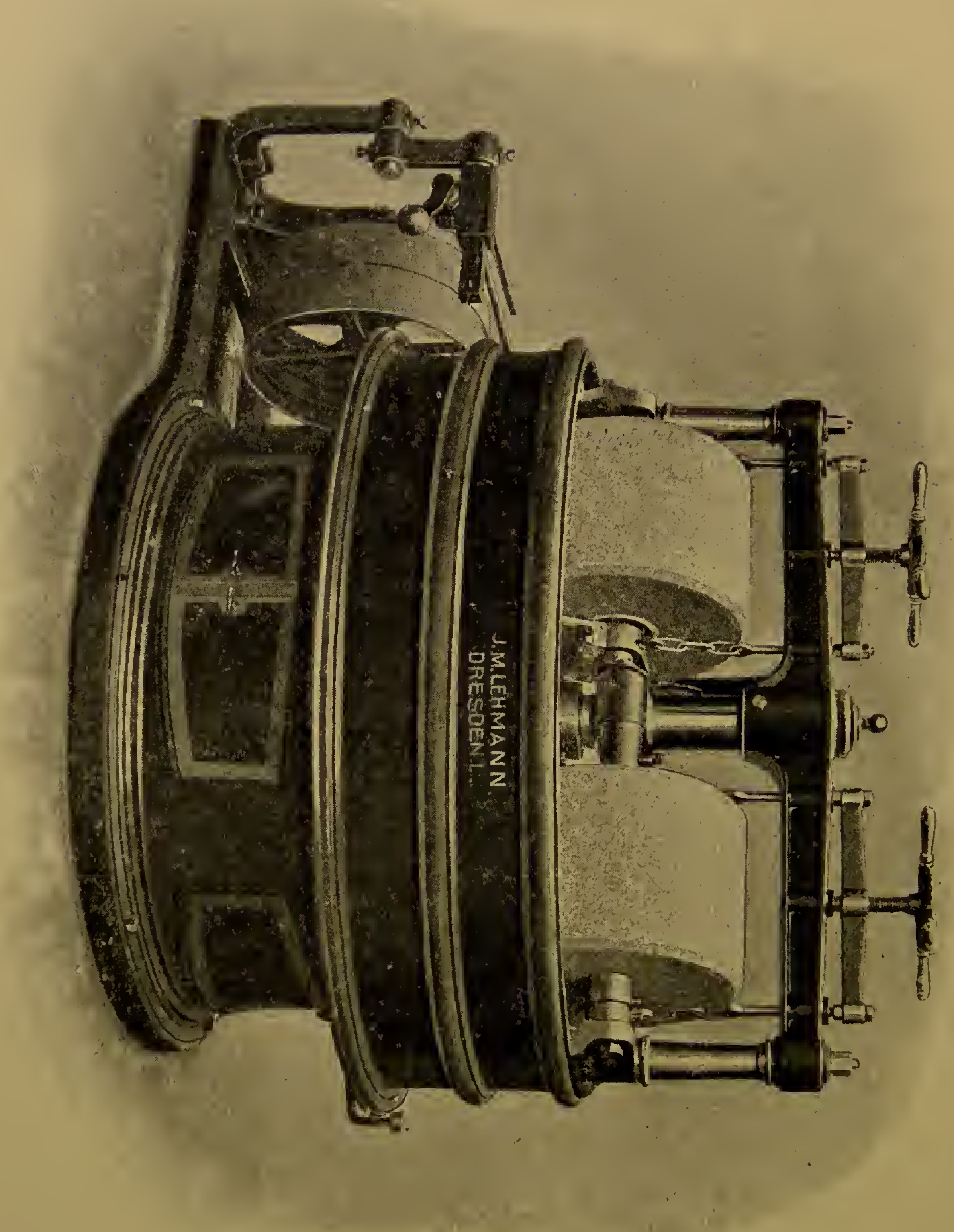
The Melangeur.

The "melangeur" illustrated, made by Messrs. Lehmann, of Dresden (Fig. 8), is admirably suited for this work. Each roller is fitted with a raising device, which enables an easier starting of the machine after stoppage, does not allow thumping of the rollers on the granite bottom of the pan, and causes an easier and more rapid grip on the larger pieces of cacao and sugar if the cacao mass is put into the pan in lumps.

The "melanguer" is capable of being heated by a steam coil placed immediately underneath, so that the pan can be quickly raised to the required temperature before introducing the charge. Such a machine, occupying a floor space of $7\frac{3}{4}$ ft. by 6 ft. and $5\frac{1}{2}$ ft. high, will cost £150, and can be obtained from Messrs. Bramigk & Co., 5, Aldgate, London, who are the sole agents for Messrs Lehmann's machinery in this country.

Iron dust-proof covers can be provided with these "melangeurs" at a little additional cost, and will often prove advantageous when the chocolate paste is run continuously in the machine for any length of time.

"Melanguers" can be bought with one or two rollers



By permission of Messrs. Bramigk & Co., London.

FIG. 8.—Chocolate "melangeur." (See p. 123.)

simple or conical shaped according to requirements, and the capacity of the machine can be made to hold a charge of anything from ½ to 3 or 4 cwt.

The dry sugar, flavouring matters and cacao paste having been well mixed in the "melangeur," the crude chocolate will be in a semi-liquid form, somewhat resembling a very soft dough. The sample will be slightly gritty to the teeth, due to the particles of sugar and the coarser grains of the milled cacao, and must undergo a refining process.

The Refiner.

Refiners consist of a series of connected rollers, which revolve at different rates of speed in opposite directions. Two or more rollers are made to work against each other, and are fitted with driving cogs, having different number of teeth. Consequently the roller connected with the wheel having the larger number of teeth revolves at a slower rate than that with the smaller number. The grinding or reducing power of the rollers is in this way brought up to a maximum.

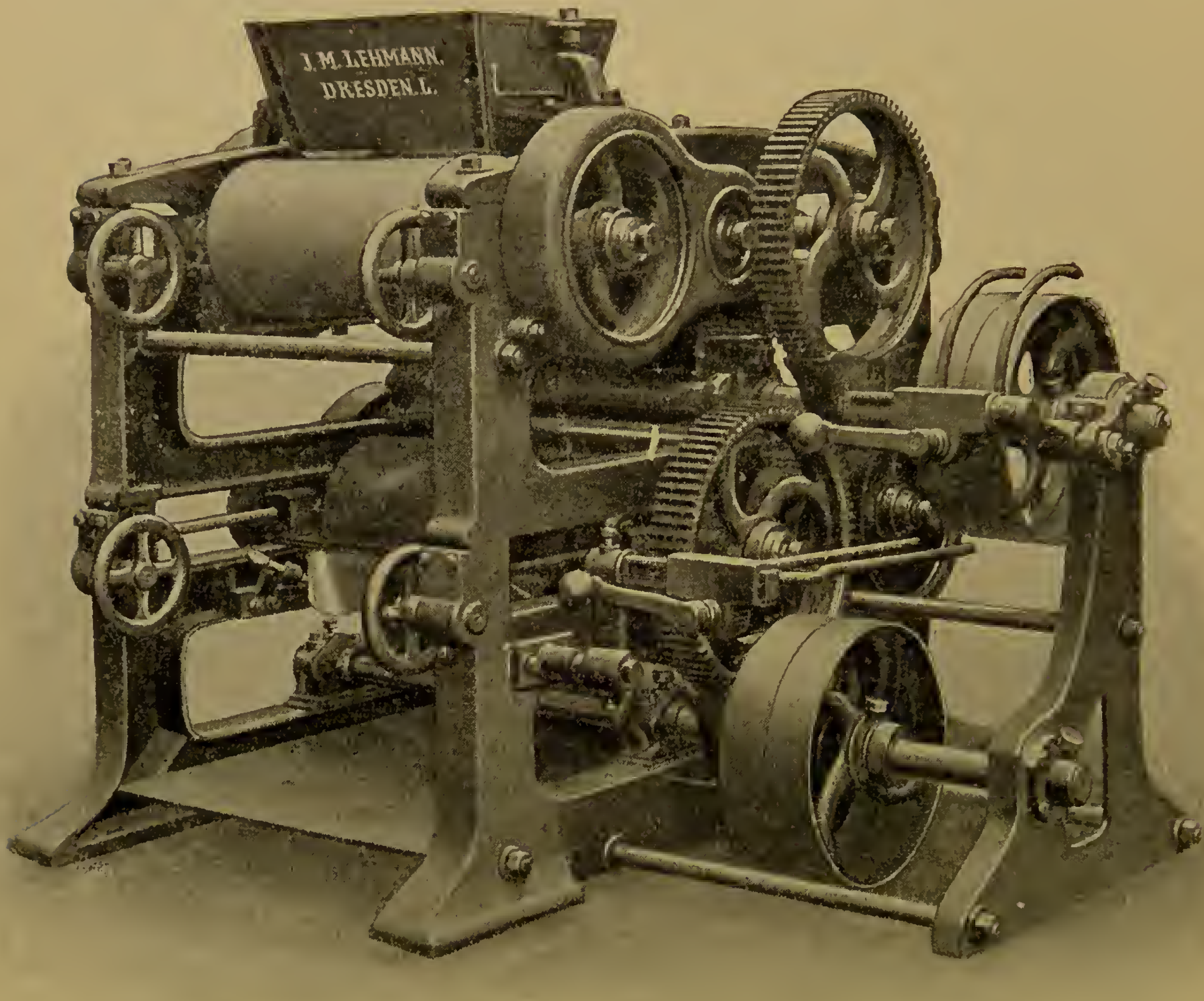
An extremely hard form of granite, diorite, has been found to be the most serviceable material with which to construct the rollers, and the quarries from which the granite is obtained are in the hands of the principal makers of chocolate machinery, such as Messrs. Lehmann.

Modern refiners have cylinders of polished chilled steel, which not only reduce the chocolate to a finer state of division in a given time than can be obtained with the granite set, but they have the additional advantage of being able to be water-cooled—a necessity which arises on the cylinders becoming heated from over-friction or continual running.

The rollers in the older-fashioned granite refiners were placed in a horizontal position, while the modern steel or

granite roller machines are upright, and the former has a parallel water-cooling system attached.

A good type of machine for refining and finishing chocolate with granite rollers in a horizontal position is



By permission of Messrs. Bramigk & Co., London.
FIG. 9.—Horizontal refining machine. (See p. 126.)

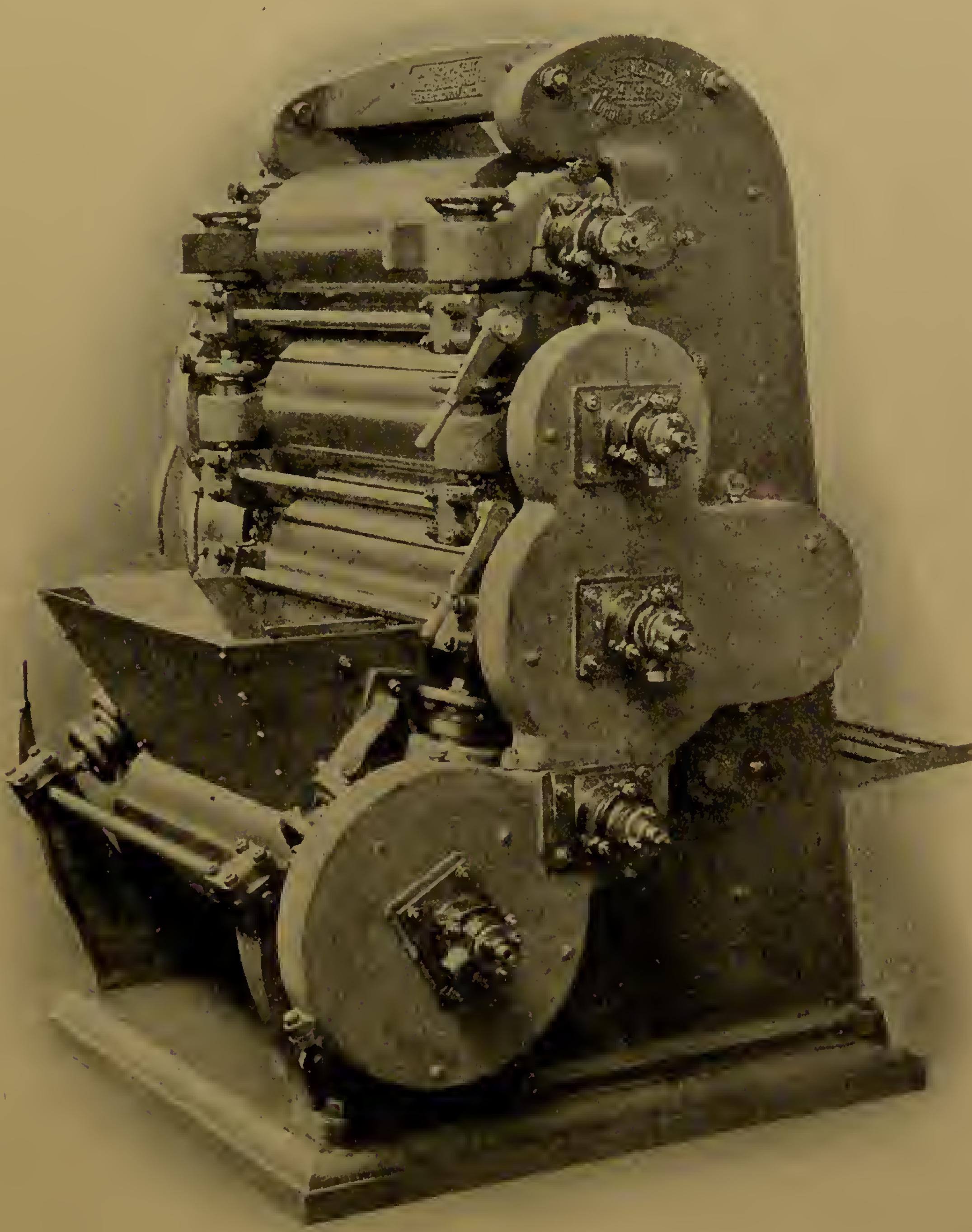
illustrated (Fig. 9), and occupies a floor space of $6\frac{1}{2}$ ft. by $6\frac{3}{4}$ ft., and a height of $6\frac{1}{4}$ ft. It can be obtained from Messrs. Bramigk and Co. for £150.

Upright steel roller refiners are now made by all makers of chocolate machinery, the one illustrated being made by Messrs. Baker and Sons (Fig. 10).

This machine has been specially designed to bring

about a higher speed, larger output, and finer grinding than could be obtained on the ordinary granite rollers.

The rollers are of chilled steel, carried on lever arms,



By permission of Messrs. J. Baker & Sons, Ltd., Willesden.
FIG. 10.—Patent five-roll upright refiner with chilled rolls and spring bearings. (See p. 126.)

with spring-bearings and hand-lever adjustment. These advantages enable a much closer adjustment of the rollers to be made, and these, being of chilled metal, are much

harder, will take a finer polish, and remain truer in use than if made of granite. The spring bearings and the fact that the cylinders or rollers are water-cooled make it possible to run the machine at high speeds, ensuring a large output and great efficiency.

The five-roll upright refiner with chilled rollers and appliances, as described, occupies a space $4\frac{1}{2}$ ft. wide by $7\frac{3}{4}$ ft. long by $6\frac{3}{4}$ ft. high, and will cost about £300.

If necessary a battery of refiners can be formed, the chocolate paste from the last roller of the first set being transferred by means of a scraper to the hopper of the next. The advantage of this system is that where a chocolate needs and can stand a second or third consecutive refining, time is saved by automatically feeding the once-refined chocolate through a second or third set of refiners, without having to wait to transfer it to pass through the same refiner a second or third time.

The chocolate mass is taken from the "melangeur" straight to the hopper of the refiner, in which the first roller is revolving slowly, carrying on its surface sufficient chocolate to transfer it to the next, which travels at a higher speed. The upper sets of rollers revolve still faster, and, being set close, grind the chocolate to a fine state. A scraper removes the chocolate from the last roller, either into pans placed beneath or into the hopper of the next set.

All chocolate, for whatever purpose it may be intended, must be passed through the refiners once or twice, the best quality of eating chocolate being refined as many as six or eight times between various "rests" given to it in the hot cupboard and further treatments in the "melangeur."

The chocolate mass after the first mixing is in a soft, doughy state, but after being passed through the refiner once is reduced to a dry, light powder, similar to cocoa powder.

This is partly the result of cooling down on the rollers,

which should never be run while hot, and partly from the crushing of the sugar particles, which tends to dry the chocolate.

In this dry, powdery state the chocolate is not in a fit condition to undergo further immediate refining, but it should be placed in a pan in the hot cupboard to recover, and then run for a short time in the "melangeur" before being again passed through the refiner.

By constant consecutive refining there is a tendency to "fatigue" the chocolate, that is to say, to reduce it to a powdery state from which it will not recover without addition of more cacao butter. This may often be the case after the first refining if too large a quantity of sugar has been used or the cacao nibs are not of a very fatty nature, but it may be avoided in after refinings by giving the cacao mass a rest in the hot cupboard, when the butter will be seen to come to the surface and will be found to permeate the whole mass once again.

There is little doubt that chocolate "fatigues" more easily on granite than water-cooled steel roller refiners, and especially so is this the case when milk chocolates, containing a great deal of body matters, are undergoing the process.

The degree to which chocolate is refined is entirely a matter of taste and requirements; that for use for covering sweets or fancy centres and biscuits requiring less refining than the finest eating chocolate, though there are many people who still prefer the coarse and gritty chocolate bars for eating purposes to the smooth and finely milled product now so common on the market.

Speed of production does not result in the highest standard of quality, and it is undoubtedly true that the treatment in the "melangeur" for an extended period enhances the flavour and consistency of the finished product, and in time would reduce the chocolate to as fine

a state of division as would be attained by the use of a refiner. This prolonged treatment, however, must be an expensive item in a factory where the machinery is driven by steam or electricity, though in a water-driven factory the cost is insignificant. In the former case, therefore, greater reliance must be placed on the efficiency of the refiner, which reduces the chocolate to a fine state in a short space of time, the "melangeur" being used for obtaining the required consistency.

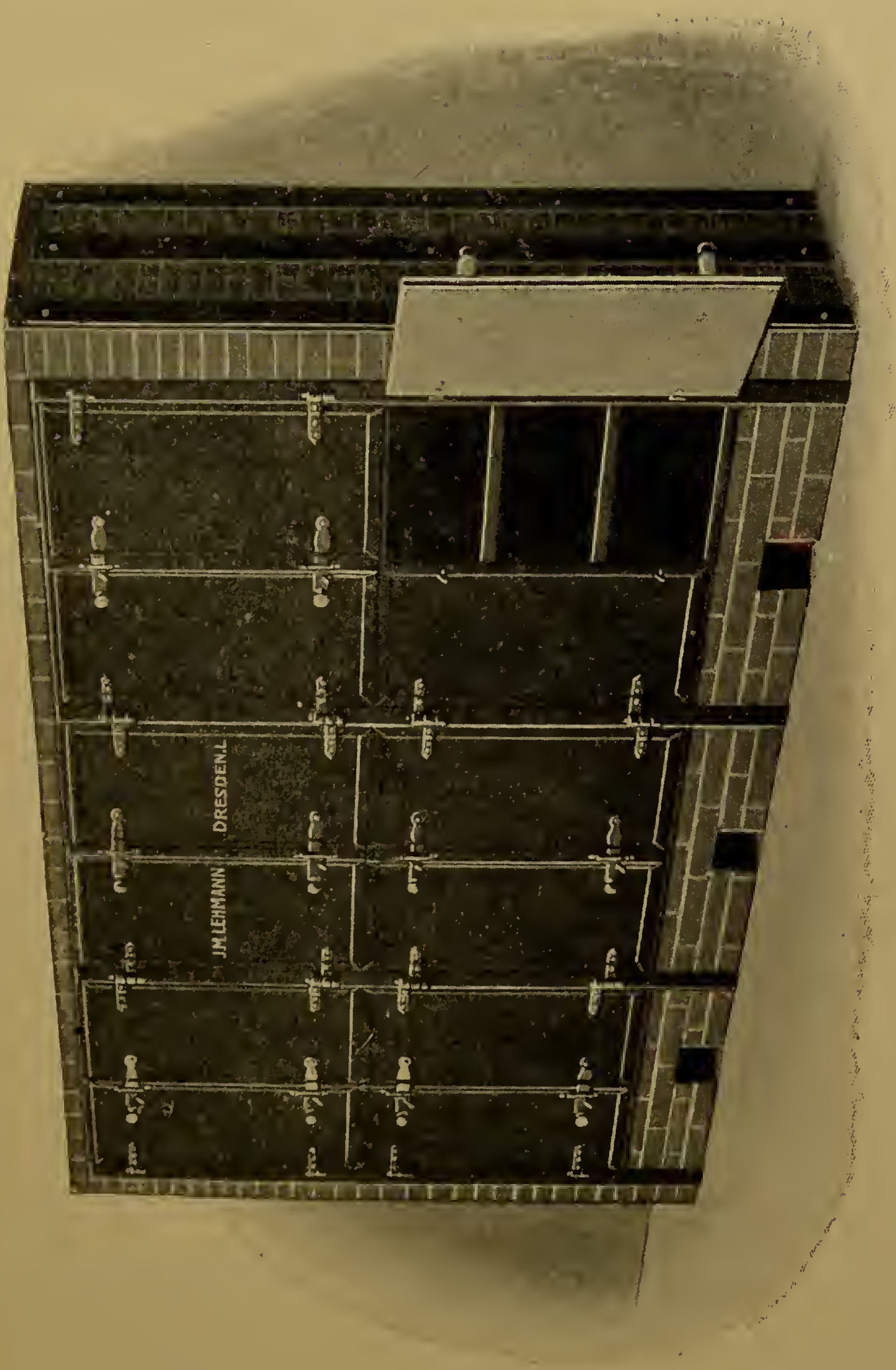
It must not be imagined that refining consists of merely running the chocolate paste through the refiners, for several important points must be considered before the required result and output can be obtained.

The judicious adjustment of the rollers is a point of no small importance, while the speed of running in the majority of chocolate factories is too rapid. Both these points must be carefully attended to, and the difficulties can be overcome by placing a skilled and competent man in charge of the refiners. The result of running the rollers at too high a speed will be the heating and drying of the paste, which, as has already been shown, can only be cured by addition of more cacao butter or prolonged treatment in the hot cupboard or the "melangeur," both remedies producing loss of profit, in ingredients, time, or labour.

The Hot Cupboard or Closet.

The hot cupboard, which has frequently been mentioned, is one of the most essential fittings of the chocolate factory.

It has already been shown that chocolate pastes, after being "fatigued" by the refiners, recover their texture after being placed in the hot cupboards or closets for a few hours. Many pastes that seem too dry ever to recover will be found to revive if left in the hot cupboard for



By permission of Messrs. Bramigk & Co., London.

Fig. 11.—Heating chamber for chocolate, etc. (See p. 132.)

twenty-four hours, and no extra addition of cacao butter will be needed.

The hot cupboard is also employed for melting cacao butter and chocolate base, and for warming the sugar, prior to mixing them in the "melangeur."

The heating chamber illustrated, made by Messrs. Lehmann (Fig. 11), consists of an iron frame with five iron shelves, and is fitted with overlapping double swing doors. The heating is effected by steam in the space at the bottom of the chamber.

In the closet in question there is a storage capacity of about 600 lbs. of chocolate to each yard of space, and the whole measures 10 ft. long by $2\frac{3}{4}$ ft. deep by $6\frac{3}{4}$ ft. high, and costs £23. For extension purposes additional lengths of $3\frac{1}{3}$ft. can be obtained at a charge of £6 15*s*. per length.

CHAPTER XV

MOULDING CHOCOLATE TABLETS, CROQUETTES, NAPOLITAINS AND FANCY SHAPES: TAPPING, COOLING

THE chocolate, after the necessary smoothness and consistency has been obtained by treatment in the "melangeur" and refiners, is placed in the hot cupboards till required for moulding. Each tin in the cupboard should be clearly marked to indicate the grade of the chocolate and date of manufacture.

It may be desirable, and is often considered a necessity, to knead the chocolate paste prior to moulding, as the temperature in the hot cupboard of 50° to 60° C. may have caused separation of the solids from the fat, which would rise to the surface.

The chocolate-kneading machine is usually a small one roller "melangeur," which may or may not require heating according to the temperature maintained in the factory and the coldness of the day.

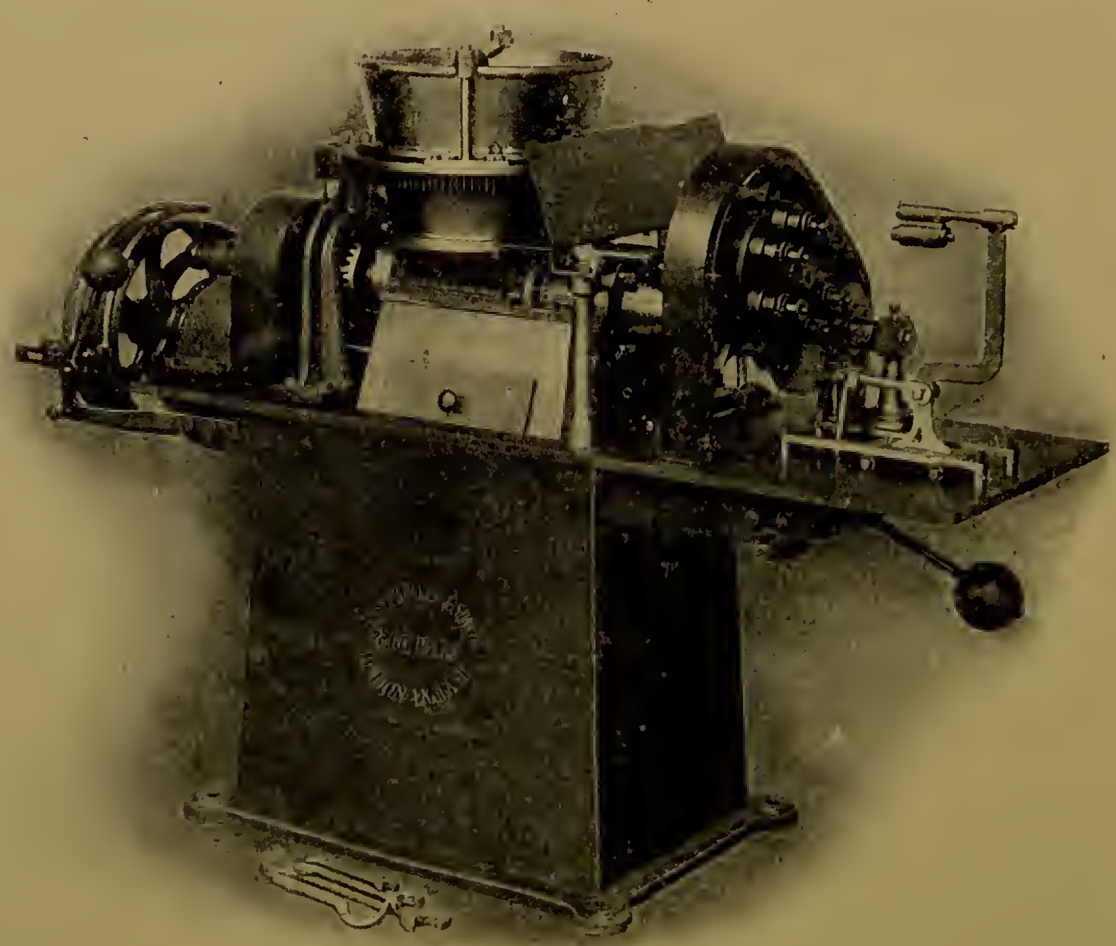
When the chocolate paste has acquired the correct consistency, which does not usually take longer than the time necessary to mix it thoroughly, it is taken from the kneading machine and placed on a wooden or marble table and spread in shallow rows.

The reason for this operation is to bring down the temperature of the chocolate paste to one reasonably low enough for passing through an air-extracting machine, automatic weigher, or other desirable and labour-saving devices, immediately prior to moulding.

Air-extracting Machine.

Where an extracting machine is employed, the chocolate, at a temperature of 32° to 33° C., must be fed into the machine warmed to a temperature similar to that of the paste.

The chocolate in passing from the hopper is forced by



By permission of Messrs. J. Baker & Sons, Ltd., Willesden.
Fig. 12.—Patent air-forcing and automatic chocolate-weighing machine. (See p. 134.)

a helical axle into a small receptacle, whence it escapes through a conical orifice and is cut by a simple device into required lengths or weights.

In the machine designed by Messrs. Baker & Sons (Fig. 12), an apparatus somewhat resembling the cartridge cylinder of a revolver is placed in front of the outlet of the

air-extracting machine, and is fitted with six tubes, in each of which works a piston. Each tube is presented in turn in front of the outlet, and as soon as filled is automatically emptied by the piston so as to deliver, if required, on to a continuous travelling band. By altering the size of the tubes the machine can be adjusted to weigh from $\frac{1}{4}$ lb. to $\frac{1}{2}$ lb., or from 1 oz. up to $\frac{1}{4}$ lb.

The cost of the machine is £140, and the overall dimensions are $5\frac{1}{4}$ ft. long by 2 ft. wide by 4 ft. high.

The air-extracting machines work very well for medium and soft pastes, but irregular and rough lengths will emerge from the outlet if the chocolate is too dry.

In many factories the air-extractor is dispensed with, especially where hard dry pastes are employed, and in such cases the chocolate is pressed directly into the clean dry moulds, when the subsequent action of the tapping table brings the air-bubbles to the top, whence they can be removed.

Moulding.

Assuming that the chocolate is ready to be moulded, whether or no it has passed through the air-extractor and weighing machines, and is at a temperature of 32° C., the paste of dry chocolates may be pressed by hand into the moulds, or, if of the softer varieties, spread with a palette knife.

The moulds should be of polished white metal, thoroughly clean and dry and warmed to the same temperature as the paste. These precautions are most necessary, as the finish of the tablet or moulded article depends entirely upon the care with which the moulds are treated. Dull spots on the surface of the finished moulded chocolate are the results of dull dirty moulds, or they may be caused by the moulds being cooler than the paste pressed into them. The grey top

surface "break" of the chocolate may also be put down to this same cause.

The correct temperature for moulding is from 30° to 32° C., though many figures have been published to show the varying temperatures for moulding at different times of the year.

Such variations of moulding temperatures should not be necessary in factories kept at a reasonably constant temperature throughout the year, say 20° C.—a matter of no great difficulty in these days of efficient heating and cooling systems.

Small tablets, however, should not be moulded below 32° C., while larger masses of chocolate will hold what heat they contain the longer, and may consequently be moulded as low as, say, 28° C.

If variations of temperature do occur in the atmosphere of the moulding room, it is obviously necessary to increase the temperature of moulding during the cold, and lower it during the hot weather. Experience is the best guide to the correct temperature for moulding during fluctuations of atmospheric temperature, though 5° C. on each side of the limits mentioned will probably meet all requirements.

It is advisable to make use of a thermometer to regulate the moulding temperature, though here again experience steps in, and it will be found that persons well versed in moulding chocolate, and especially those who are constantly handling the same variety, can tell as accurately as any thermometer when the correct temperature has been reached by the feel of the consistency of the paste or by the heat of the chocolate felt on the lip.

If the chocolate is to be sold by weight and to be moulded, the weighed paste is pressed evenly over the mould; if merely in tablets without a guaranteed weight, sufficient paste to fill the mould is pressed or filled in with

a palette knife, and the surplus chocolate removed by running the knife over the surface of the mould.

The Tapping Table or Shaker.

The chocolate-filled moulds are then placed on the tapping table, an apparatus which, by means of a roughly toothed wheel placed beneath the table surface, is given a rapid and violent vibrating movement, and consequently the moulds placed thereon suffer the same treatment. The effect of this is to cause the chocolate to run into every corner of the mould, completely filling it, and by coming into close contact with the polished metal the chocolate is given a high polish when cold. Any bubbles which may be retained in the paste are brought to the top, and may be removed by a knife, or by breaking them with the tip of the finger.

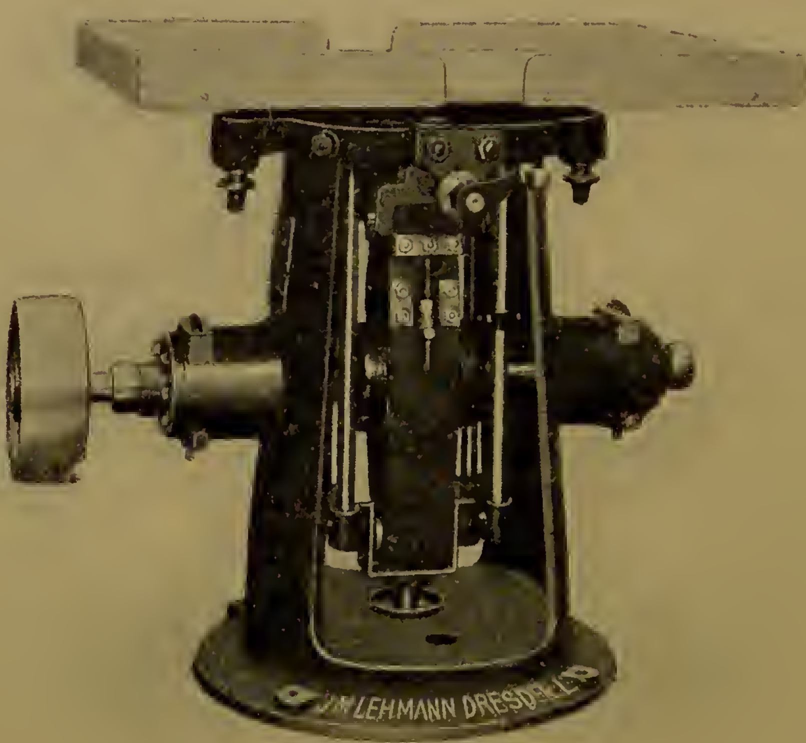
The noise created by the bumping of the table top and of the moulds upon it is very considerable, and where many tapping tables are at work it becomes deafening. There are now fortunately on the market noiseless tapping tables which reduce the greater part of this inconvenience, with the exception of the noise cause by the moulds themselves. The clattering of the moulds cannot be obviated, as it is necessary to jar them continuously and violently, a result which could not be obtained if a felt or other silencer were placed upon the table.

The tables are adjusted so as to administer anything from a very heavy shaking down to the merest vibration, so that all sizes of moulds, containing the thickest to the thinnest tablets of chocolate, from hard dry paste to the most liquid, can be efficiently shaken into the moulds and freed from bubbles.

The cost of a tapping table (Fig. 13), noiseless and adjustable, 3 ft. long, 2 ft. wide, and 3 ft. high, will cost

from £25 to £30, and can be obtained from any maker of chocolate machinery.

All the larger tablets of chocolate, such as bars, croquettes, napolitains, etc., are moulded in the method described, the smaller chocolate drops, shells, and other small fancy shapes requiring a special system of moulding to increase the rate of production.



By permission of Messrs. Bramigk & Co., London.
FIG. 13.—Noiseless shaking table. (See p. 137.)

The moulds for the larger sizes of chocolate tablets are made of heavy, specially tinned and polished metal, or of white metal, and contain from two to twenty-four impressions, according to the size of the tablet required, while the chocolate drops or designs of similar size are stamped out in light tin of much larger dimensions than the heavier moulds, containing as many as twelve dozen impressions.

Drop Press Machine.

Small mouldings and even napolitains and croquettes are with advantage made on the drop press, which mainly consists of a square vessel to hold the chocolate, and into which fits a plunger worked by a screw with a turning wheel attached. The bottom of the vessel is fitted with a removable perforated bottom, the position of the holes corresponding to the impressions of the mould, which is slipped in underneath. After the chocolate has been placed into the receptacle warmed to the correct temperature, the plunger is lowered by the turning wheel, and when gentle pressure is felt on the chocolate mass, a small quantity of the paste is forced through the perforations of the bottom into the corresponding impressions of the mould.

The surplus chocolate is removed from the mould plate with a scraper, and the chocolate-filled moulds are placed on the tapping table. In this way a very large number of moulds can be filled in a short time, and at a much greater speed than by hand-filling.

By so arranging the drop press the chocolate can be made to deposit on plain sheets of tin in drops of any size, and can be caused to assume a symmetrical, thin and flattened shape by placing the sheet on the tapping table.

The drops can be covered, if desired, with coloured sugar or "hundreds and thousands" before being placed in the cooling chamber.

The cost of a drop press is £13 to £14.

Continuous Mould-filling and Tapping Machine.

An ingenious mould-filling machine, combined with a continuous tapping table, which accurately divides and deposits both hard and soft pastes into the moulds, has been introduced by Messrs. Baker & Sons.

At the top of the machine, and situated at one end, is a hopper, water jacketed, so that the chocolate can be maintained at the correct temperature for moulding. A pair of adjustable rollers are fitted beneath the hopper, which deliver the chocolate to a set of dies, so made that they will fill a mould of any shape with the exact amount of chocolate.

The machine is further capable of being adjusted and regulated whilst running to deliver any required weight of paste. When the moulds are filled they are carried by chains over a series of tapping tables, which, by exceedingly rapid vibrations, settle the chocolate quickly and evenly in the moulds. This rapid movement has been found more effective than the hard knocking motion of the ordinary shakers.

If required, a cooler can be attached to the end of the machine, so that the moulds containing the chocolate can be continuously tapped and cooled, and delivered at the end in a state fit for knocking out.

Chocolate Coolers.

When the moulds have been filled and tapped, they should be cooled down so as to harden the chocolate for knocking out. It has been shown by experience that the texture and appearance of moulded chocolate are improved by rapid cooling—facts which are probably due to the formation of small crystals of cacao butter when rapidly cooled, whereas slow cooling would produce larger and coarser crystalline formation. On the other hand, there are greater dangers in too rapid cooling if the utmost care is not taken to prevent the condensation of moisture on the chocolate, which will occur if the cold tablets are taken into a warmer and moister room immediately from the cooling chamber. The deposition of moisture may also

take place in the cold room itself if the air is not kept dry by keeping the chamber closed as much as possible.

It is true that the majority of firms make use of artificially cooled rooms, in which the temperature is not allowed to rise above zero, mainly for the purpose of accelerating the cooling process, but better, safer and more consistent results will be obtained if a room kept constantly at a low temperature of, say, 10° C. is employed for cooling down the chocolate.

In winter months this should not be difficult to obtain, but in the warmer summer days artificial cooling would have to be resorted to, unless the room were situated well below the level of the ground.

There are many systems for producing low temperatures artificially, and they are all based upon the principle of absorption of heat when a volatile liquid or an easily compressible gas is allowed to expand to the gaseous state. The cold so created may be allowed to act directly upon the cooling chamber, or to be imparted to solutions of salts, such as of calcium chloride, which, flowing through pipes in and around the chamber, quickly lower the temperaure.

Liquid ammonia, carbonic acid, and sulphurous acid are chiefly used for producing the cold, and by a system of alternate expansion and compression the volatile liquids are reduced first to the gaseous state, and then back to the liquid form, the result of the first process being allowed to react in the neighbourhood of the cooling chamber, or upon the brine solution, without loss or escape of the gases.

For large cooling chambers the brine and ammonia system is most economical. The brine may either circulate in pipes around the chamber, or be in turn deprived of its chill by a strong draught of air blowing through it as it falls over the cold ammonia pipes.

In smaller factories, where the cooling requirements are not so great, the carbonic and sulphurous acid system, coupled with circulating brine, will be found to be the most serviceable and efficient, and to occupy only a small space.

An excellent cooling system, designed by Messrs. Cole and Co., in which air is compressed, cooled by circulating water, and then allowed to expand, gives very good results. The cold air is dried and used directly for cooling down the chamber in which the chocolate-filled moulds are placed, or it may be conveyed through thoroughly insulated pipes to any part of the factory required. The drying of the cold air acts as a safeguard against condensation of moisture on the surface of the chocolate, though the same danger by removing the cold-filled moulds to a warmer, moister room will still be incurred.

To obviate this, it is desirable to bring the temperature of the moulds slowly up to that of the factory, either by passing them on a slow travelling band through chambers of steadily increasing temperature, or by placing them in a room at a temperature between that of the cold room and factory for a short time prior to knocking the chocolate from the moulds.

When the chocolate and moulds have attained the normal temperature of the factory, the moulds should be slightly bent backwards or gently tapped to remove the contents, which may then be packed in tinfoil and wrapper, ready for the market.

The moulds should never be struck hard to remove the chocolate, and if moulded at the correct temperature there will be no need, for the tablets will fall out without tapping.

If too high a temperature has been employed during moulding, the chocolate will stick tight to the mould, and the surface will be spotted with dull patches; if moulded too cold, the surface will be whitish and marbled.

During cooling, the chocolate contracts and generates frictional electricity, which has been attributed to the rubbing of the particles of chocolate on the metallic surface of the mould containing it. A certain Mr. Sanders, a chocolate maker, observed this, and found that by continually heating and cooling the chocolate, the power of generation of electricity gradually disappeared, but that it could be restored by addition of a small quantity of olive oil.

CHAPTER XVI

ANALYSES OF PLAIN CHOCOLATES, EATING, COVERING, AND POWDERS

Plain chocolates, the preparation of which has been described in the foregoing chapters, should consist only of roasted and shelled cacao beans, sugar, small quantities of flavouring matters, and added cacao butter.

Booth has frequently pointed out the need for a definition of chocolate in England, and has strongly advocated that the addition of starch and fats, other than those naturally present in the cacao bean, and of shell powder, should be absolutely excluded from any article which is to be sold under the name of "chocolate."

The limit of 65 per cent. of sugar has also been suggested, but at present, as there is no legal standard for chocolate, the analyses of several well-known brands are perhaps the best guide as to what chocolate should be.

The quality of a chocolate does not, however, entirely depend upon its chemical composition, but largely also upon the degree of fineness to which the chocolate has been ground, and which gives that pleasant smoothness so much appreciated by the chocolate-eating public of the present day.

On the other hand, were it not for the careful attention given to chemical analysis, the public might still be suffering in the same way as in the days of Hassall, and it would seem that there is the greater need for definite

legislation on the subject now, as the methods of adulteration are far more subtle than in Hassall's time.

In reading Hassall on 'Food and its Adulteration,' published in 1876, one cannot fail to be struck by the amazing frauds that existed at that time, if all he writes be correct, and of the remarkable improvements in the nature of our food-stuffs made in the last thirty-five years.

In quoting from the work of Normandy, he says: "Unfortunately, however, many of the preparations of the cocoa-nut (cacao bean) sold under the names of chocolate, of cocoa flakes and of chocolate powder, consist of a most disgusting mixture of bad or musty cocoa-nuts, with their shells, coarse sugar of the very lowest quality, ground with potato starch, old sea-biscuits, coarse branny flour, animal fat (generally tallow, or even greeves). I have known cocoa powder made of potato starch moistened with a decoction of cocoa-nut shells, and sweetened with treacle; chocolate made of the same materials with the addition of tallow and of ochre. I have also met with chocolate in which brick dust or red ochre had been introduced to the extent of 12 per cent.: another sample contained 22 per cent. of peroxide of iron, the rest being starch, cocoa-nuts with their shells and tallow.

"Messrs. Jules Garnier and Harel assert that cinnabar and red lead have been found in certain samples of chocolate, and that serious accidents have been caused by that diabolical adulteration."

Hassall himself, from the examination of twelve samples, found added starch in eight of them, ranging from 10 per cent. of sago starch to 30 per cent. of wheat flour, besides a large proportion of sugar. He says: "Besides the above ingredients, several of the chocolates contained coloured ferruginous earths," and admits that as chocolate is a compound article, there can be no valid objection to the inclusion of sugar and starch, provided

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the composition is acknowledged, the main points to be considered being the price of the article and the proportions and quality of the ingredients of which it is composed.

It is safe to say that in these days, with the exception of chocolate powders and the very cheapest eating chocolates, even the admixture of starch is unknown, while animal fats and added mineral matters are never met with as adulterants.

Shell powder or husk is a fairly common adulterant still, and cacao butter substitutes may be frequently found in chocolates, though it is seldom that the latter are employed unless it is required to harden, as well as to cheapen, the material.

The majority of books quoting the adulterants of cocoa and chocolate still include, besides sugar and starch, Venetian red, cinnabar, brick dust and peroxide of iron, oil of almonds, cocoa-nut fat, beef and mutton fat. With the severe competition among chocolate manufacturers of the present day, it would be madness to make use of the mineral matters enumerated for colouring purposes or loading, as their presence if detected would condemn for ever the products of the factory from which such chocolate emanated.

Oil of almonds would not be added as an adulterant, firstly, because of its high price, secondly, because of its low solidifying point, and thirdly, because in the best French and some English chocolates a small quantity of powdered almonds or hazel nuts is included to produce characteristic flavour, and their presence cannot in any way be looked upon as adulteration if small quantities of harmless flavouring matter is permissible in chocolate.

Cocoa-nut fat may possibly be found in some chocolates, and it is probable that its inclusion will become more general if the increasing market value of cacao butter

continues. In itself cocoa-nut fat is harmless and pleasant, but in chocolate it is undoubtedly an adulterant. The melting-point of cocoa-nut fat is somewhat lower than cacao butter, and it does not possess the same body. It would therefore be included for no other purpose than cheapening the chocolate, as it would not impart hardening qualities.

Beef and mutton fat are not likely to be found in chocolate, as the combination of animal fats and cacao butter do not keep well, and after the chocolate containing either of these animal fats has remained in stock for a short time it will acquire a tallowy taste, which will predominate over the aromatic flavour of the cacao.

It is, however, desirable to be prepared to meet with any possible adulterant, and the methods of detection of any added matter found in chocolate to date will be discussed in the third part of the book.

Booth* has made a careful study of the analysis of chocolates, and as the results obtained are interesting and valuable, a few of them are here included:

TABLE XXV.—*Analyses of some Plain Chocolates.*

	I.	II.	III.	IV.	V.	VI.	Average of 24 samples.
Fat	34·6	33·6	25·6	22·1	28·1	23·7	27·4
Sucrose	46·0	50·5	53·0	54·0	52·2	54·0	53·4
Nitrogen	0·86	0·81	0·86	0·92	1·14	1·05	0·93
Mineral matter	1·45	1·05	1·41	1·22	1·50	1·48	1·32
Cold water extract	50·0	54·8	56·9	58·1	58·2	58·9	56·8

These figures show merely the fluctuation in the composition of chocolate due to the presence of different quantities of added sugar and cacao butter, and are typical of the majority of better-class hard chocolates on the market.

The same author has, however, analysed several adulterated chocolates, with the following results:

* N. P. Booth, 'The Analyst,' 1909, xxxiv, 145.

TABLE XXVI.—*Analyses of some Adulterated Plain Chocolates.*

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Moisture . . .	1·8	0·8	1·1	1·2	3·03	1·2	3·8	3·6
Mineral matter. .	1·04	1·01	1·03	1·96	2·13	0·85	0·88	1·05
Fat	25·9	23·0	23·3	30·7	32·93	29·8	27·2	24·35
Sucrose . .	48·0	56·0	56·0	44·0	46 0	47·0	40·0	—
Foreign starch . .	15·0	8·0	7·5	20·0	*Nil*	10·0	20 0	—
Character of starch .	Arrow-root	Wheat	Wheat	Maize	—	Arrow-root	Arrow-root	Sago
Fat-free cocoa matter	10 0	12·0	12·2	8·3	20·6	12·0	8 4	—
Fibre (calculated on fat-free cocoa matter) . . .	8·7	10·0	9·8	16·6	4·5	8·5	10·0	8·8

The high percentage of mineral matter in sample IV is attributed to the addition of red ochre, and the 32·93 per cent. fat found in V consisted mainly of foreign fat.

It is impossible to fly in the face of these recorded figures, and to say that all chocolates are free from adulteration of added mineral matter and foreign fats, but it is our experience that the majority of chocolates on the market are remarkably pure, with the exception of occasional addition of starch and cacao butter substitutes, which are usually of vegetable origin, and of the careless or intentional inclusion of cocoa husk or shell powder.

Those chocolates with under 30 per cent. of fat were probably of the dry variety, as the large proportion of sugar present, amounting to over 50 per cent. of the chocolate, would have the tendency to dry up the existing fat, and render them more suitable for the preparation of chocolate powders.

Chocolates containing 60 per cent. of sugar would be incapable of being moulded without further addition of cacao butter.

Génin* has divided his analyses under the headings of

* M. V. Génin, 'Encyc. Chimique,' x, 4, 504.

German, French and Spanish chocolates, and his results are collected in Table XXVII:

TABLE XXVII.—*Analyses of some Plain Chocolates.*

	German.	French.	Spanish.
Moisture	1·88–2·50	0·98–1·28	1·20–1·50
Fat	22·50–28·55	21·40–23·80	20·50–26·60
Nitrogenous matter	5·81–8·18	4·57–4·99	6·45–8·67
Theobromine	0·56–0·80	1·26–1·43	1·82–2·64
Sucrose	37·86–55·31	56·34–59·07	41·40–54·0
Starch	4·44–6·49	0·97–1·83	1·33–1·74
Cellulose	0·70–2·10	—	—
Ash	1·44–2·01	1·75–1·87	2·43–3·23

From these figures it would appear that the French favour the driest and sweetest chocolate, the Germans preferring those more fatty. It is a pity that no figures are given for cellulose in the Spanish chocolates, as the high percentage of ash therein would indicate that there is a larger percentage of husk included in them than in the others. As the figures stand, and without the cellulose values, the high ash content may be due to some treatment of the beans with fixed alkali, or some other mineral or mineral-containing matter, for purposes of improving the flavour of the chocolate.

Chocolate powders, such as all makers now produce, usually contain from 20–25 per cent. of fat and 50–60 per cent. of sugar, with the addition of foreign starch in the majority of cases, to add to the thickening property of the beverage and to the maintenance of the chocolate in a fine powdered form.

Ewell* gives the following analyses of some commercial chocolate powders:

* E. E. Ewell, 'U.S. Dept. of Agriculture,' Bull. 1".

TABLE XXVIII.—*Analyses of some Commercial Chocolate Powders.*

	Rowntree's powdered chocolate.	Epps's prepared cocoa.	Fry's diamond sweet chocolate.	Chocolat menier.
Fat	25·84	25·94	18·60	21·31
Fibre . . .	1·30	1·51	0·81	1·10
Sucrose . . .	51·0	26·0	55·0	58·0
Ash	1·66	3·15	1·16	1·40
Added starch . .	Very small amount of arrowroot	Much arrowroot	Much wheat starch, some arrowroot	*Nil*

Bell* gives an analysis of several preparations of cocoa, such as Iceland Moss Cocoa, Rock Cocoa, Flake Cocoa, and Chocolat de Santé, which consist of 2·5–5·5 per cent. of moisture, 17–25 per cent. of fat, *nil* to 25 per cent. of added starch, and *nil* to 61 per cent. of added sugar. These preparations are seldom met with now, and are of little or no commercial importance.

Smooth fatty chocolates, called in France "chocolats fondants," have taken the popular fancy very considerably in the last few years.

This may be due to the popularity enjoyed by milk chocolates, which are smooth to the palate.

There is no secret in the composition of these chocolates, which owe their character entirely to the method of manufacture and to the extra quantity of cacao butter which they contain. The method for their manufacture is described in the next chapter.

Another important feature of the chocolates of the smooth fatty variety is the extreme fineness to which they are ground, a condition which is only reached by continual working in a "melangeur" or "conche" machine and frequent refining.

An analysis of "Meltis," manufactured by Messrs. Peek,

* J. Bell, 'The Chemistry of Foods,' 1881, 89.

Frean & Co., Ltd., and which has been taken as typical of a high-class chocolate of this variety, is given:

Analysis of "Meltis"—"Chocolat Fondant."

Moisture	1·45	per cent.
Sugar	57·33	,,
Cacao butter . . .	33·68	,,
Nitrogen	0·745	,,
Ash	0·98	,,
Added starch . . .	*Nil*	
Cacao husk	*Nil.*	

The cacao butter was found to be the natural fat of cacao and free from all substitutes. Under the microscope the sugar was seen to be in an extremely fine state of division, and the mass was entirely free from husk or added starch.

CHAPTER XVII

RECIPES FOR MAKING CHOCOLATES, PLAIN, EATING, COVERING, AND POWDERS

From the analysis of a chocolate it is very easy to reconstruct one possessing the same chemical composition, but it is exceedingly difficult without much experience to determine how a special flavour or aroma is obtained.

This is obvious, seeing that different methods in manufacture will give different aromatic qualities to the cocoa, and that small quantities of an essential oil blending with the natural aroma of the cacao will completely alter the flavour of a chocolate.*

Treatment with alkali will give a certain result, and chocolate so prepared can be detected by analysis, but the blending of different varieties of beans, which is of high importance in chocolate-making, and the addition of a drop or two of an essential oil to a hundredweight of chocolate, cannot be so determined.

Various flavours, such as vanilla, cinnamon, and other spices, coffee, oil of coriander and other aromatic bodies, combine so well with cacao that nearly every manufacturer of chocolate has some secret condiment or blend of flavouring matters, with which to give his products a character, and which he claims to give a unique result.

Each country may be said to have its fancy in flavour: France prefers its chocolate mixed with almonds, hazel-

* *Vide* Chapter XIX.

nuts or chestnuts in small quantities, to give a nutty flavour, Spain likes spiced chocolate, while England favours vanilla flavour. Every country, moreover, has a slightly different variety of beans to select from, and the characteristic flavours of the varieties of cacao beans, which have already been dealt with, play no small part in determining the final flavour of the resulting chocolate.

It is not intended to give a very long list of possible blends of cacao, for it might be endless, but a few selected recipes of known worth have been chosen.

French Recipes.

Recipe 1. (*Emile Duval in 'Confiserie Moderne.'*)

	lbs.	ozs.
Ariba	2	3
Para	3	4
Machala	2	3
Large nibs	20	12
Almonds	1	2
Hazel-nuts	4	6
Cacao butter	1	2
Chestnut sugar	38	4
Ordinary ,, ...	16	0
Vanilline ,, ...	0	2
Ordinary ,, (second addition) .	10	10
	100	0

The figures are somewhat awkward, but they have been obtained from an original recipe and increased to total 100, so that estimation of the percentage of cocoa, fat and sugar can be readily made.

The chestnut sugar in the above recipe is prepared by boiling the waste syrup, after the chestnuts for "Marrons Glacés" have been crystallised in it, to 145° C.; the sugar

is then briskly stirred, so as to cause granulation and a sandy consistency ("sablé"), and dried in a drying room prior to adding it to the chocolate. The sugar, which, owing to its dark colour, has no other application in confectionery, is with advantage used in chocolate for its nutty flavour.

The chocolate from this recipe is one of the dry variety, and for this reason the whole of the sugar should not be added at once, but, after the first portion has been worked into the cacao paste in the "melangeur," the mixture is placed in a pan in the hot cupboard to recover its softness. The rest of the sugar ("sucre au revient") is then added, and the whole well worked again in the "melangeur," refined to the required smoothness, and moulded. This is not a chocolate of finest quality.

Recipe 2.

Caracas	$18\frac{3}{4}$ lbs.
Maragnan	$18\frac{3}{4}$,,
Hazel-nuts	$3\frac{1}{4}$,,
Sugar	59 ,,
Vanilla	$\frac{1}{4}$,,
	100 lbs.

Recipe 3.

Caracas	$16\frac{1}{4}$ lbs.
Para	$9\frac{1}{4}$,,
Trinidad	$18\frac{1}{2}$,,
Sugar	$55\frac{3}{4}$,,
Vanilla	$\frac{1}{4}$,,
	100 lbs.

It is needless to enumerate more of such recipes, the last mentioned being typical of the best chocolate of the

dry variety. If such a chocolate were well milled it could not be surpassed, the blend of Caracas, Para and Trinidad beans being ideal for flavour, while the percentage of sugar is not too high.

German Recipes.

Recipe 1.

Cacao mass	49 lbs.
Sugar	49 ,,
Cinnamon	$1\frac{1}{2}$,,
Vanilla	$\frac{1}{2}$,,
	100 lbs.

Recipe 2.

Cacao mass	39 lbs.
Sugar	59 ,,
Cinnamon	$1\frac{1}{2}$,,
Cloves	$\frac{1}{2}$,,
	100 lbs.

The cacao mass should consist of the better quality beans, such as Caracas, Ariba or Puerto Cabello, for the finest chocolate, though each maker has his own secret blend.

Zipperer gives a list of several working formulæ, such as one part each of Caracas and Guayaquil, one part each of Maracaibo and Maragnan, one part of Caracas to five parts Maragnan, and so on.

In the second recipe there is little doubt that additional cacao butter would have to be added to facilitate working, as the large proportion of sugar would tend to dry the paste.

Spanish Recipes.

Recipe 1.

Puerto Cabello . . .	26 lbs.
Caracas	18 ,,
Cuba	12 ,,
Sugar	44 ,,
Cinnamon . . .	to flavour
	100 lbs.

Jacoutot, speaking of this recipe, says: "Spanish chocolate is roasted in a special manner. It is its imperfect roasting which gives it the peculiar strong flavour which distinguishes it." The same author recommends that the cacao be first washed in warm water, and then boiled with the sugar and sufficient water till the sugar rises in the pan. The pan is then removed, and the whole grained in the usual manner, as for Praliné. The graining mass is loosely powdered and dried or worked in the "melangeur" and refiners till free from moisture.

This process is, however, laborious, and good results can be obtained by using half-roasted cacao and treating in the same way as for ordinary chocolate.

Recipe 2.

Cacao mass	48 lbs.
Sugar	$51\frac{3}{4}$,,
Spices	$\frac{1}{4}$,,
	100 lbs.

The spices are composed of 3 parts of cinnamon, 1 part cloves, 2 parts cardamoms, 1 part mace, and 1 part vanilla.

For other recipes of plain eating chocolates it is

suggested that works on confectionery be consulted, the only purpose served by including here those recipes already given being to show the possibility of obtaining good flavoured chocolate by special blends of beans and aromatic spices, and to give the proportions of sugar to cacao that are usually employed.

Chocolates which have been treated with alkali during the roasting of the beans, or in the process of manufacture, should perhaps be included under the heading "plain."

In the former case the method of procedure is the same as for rendering cocoa powder "soluble"; while in the latter case a strong solution of caustic soda or potash is added to the chocolate paste while running in the "melangeur," and is with advantage added prior to the first refining. If the chocolate is so treated, the greatest care should be taken to free it from moisture before moulding, and consequently the smallest possible quantity of water should be employed for making the alkaline solution.

In some factories in Switzerland and Germany the chocolate is treated with alkali, as it is believed that the flavour is improved thereby. This, however, is a matter of some difference of opinion, and it is our experience that the chocolate of finest flavour is prepared by using the best quality beans, properly roasted, without any further treatment.

In those factories where alkali is employed the caustic soda or potash is dissolved in the minimum quantity of water and added to the chocolate paste in the proportion of $\frac{1}{2}$ lb. to $\frac{3}{4}$ lb. alkali to 100 lbs. of cacao paste. It is sometimes customary to add the alkali to the cacao mass before the addition of the sugar, and to dry off the moisture in a vacuum mixer, when the sugar and other matters are added at a later stage. In either case, after the paste has been dried out, the method of procedure is the same as for ordinary chocolate.

Since the introduction of milk chocolate, the smoothness characteristic of them is expected by the public in plain chocolates. The dry, hard chocolates are not so popular as the smooth fatty varieties ("chocolats fondants") with the general public at the present day.

To meet their requirements chocolate manufacturers have been compelled to introduce a confection containing 30 per cent. and upwards of cacao butter to replace the dry chocolates of 25 per cent. fat content. To this end cacao butter is added to the recipes of the older-fashioned drier chocolates and the chocolate mass is refined to a much greater extent than formerly.

The "conche" machine, described later when dealing with milk chocolates, usually replaces the "melangeur" for mixing these smooth fatty chocolates, and the mass, after being closely refined, is worked from thirty to forty hours consecutively, and sometimes for a longer time, to acquire the characteristic "fondant" nature which is so pleasant to the palate.

Swiss chocolate manufacturers, whose work is simplified by the hydraulic power at their command, run the machines day and night, carrying the manufacture of "chocolat fondant" to the end without any interruption. This continuous process gives the consistency, while the extreme fineness resulting from close refining produces the smoothness, both characteristic qualities of this class of chocolate.

"Chocolats fondants" are, of course, more costly to produce, owing to the amount of labour and power expended, and to the larger amount of costly cacao butter used in their preparation.

The cacao butter employed is purchased on the market, and is the outcome or by-product of factories where cocoa powders are more largely produced than chocolate, in the preparation of which the surplus cacao butter, expressed

in powder manufacturing, could be employed. The fatty eating chocolates more nearly approach in composition those used for covering fondants, various sweetmeats and biscuits, though for the tablet chocolates greater care has to be taken that the finest varieties of bean are used, and that refinement is carried to the furthest degree.

Thus, "covering" chocolate, which must necessarily be of a liquid nature to ensure an even coating on the goods to be covered, is prepared by adding 10 to 20 per cent. of cacao butter to ordinary chocolate pastes, and may be embodied in a recipe as follows:

Covering Chocolate.

Cacao mass	30 lbs.
Sugar	55½ „
Cacao butter	14 „
Vanilla	½ „
	100 lbs.

Such a chocolate would show about 29 per cent. of cacao butter on analysis, while a good eating chocolate may be prepared from the following recipe, which would yield some 32 per cent. of fat on extraction:

A Modern Fatty Chocolate.

Caracas	10 lbs.
Trinidad	10 „
Para	10 „
Sugar	52 „
Cacao butter	17½ „
Vanilla	½ „
	100 lbs.

Examination under the microscope will show the extent to which the paste has been refined, though a coarse-

ground chocolate will be at once felt to be gritty under the teeth.

Chocolate fancy goods are frequently to be found in confectionery shops with a covering of milk, nut or almond-flavoured chocolate, for the preparation of which any of the special recipes reproduced in later chapters may be used, though it is probable that more cacao butter will have to be added to obtain the liquid consistency necessary for "covering" chocolate.

Owing to the high price of cacao butter its substitutes are frequently employed. Their use cannot be altogether condemned, as they usually consist of pure cocoanut or palm fat, which are quite as pure and palatable as the cacao butter of commerce.

Emile Duval points out that the use of palm butter adds solidity to a "covering" chocolate made with almonds, the oil of which has a tendency to lower the melting-point of the combined fats. This advantage is questionable as a point of superiority of palm over cacao butter, seeing that the latter has the slightly higher melting-point, though it is admitted that substitutes for cacao butter, where used, are better employed in "covering" than in "tablet" chocolate.

Chocolate Powders.

As distinct from cocoa, chocolate powders are for the most part put upon the market as a *cheap* cacao preparation for drinking purposes.

In the previous chapter some analyses of chocolate powders have been shown, and the addition of starch, besides that of sugar, common to eating chocolate, has been noted.

The addition of starch cannot be condemned if the public are fully aware that they are purchasing that commodity, as well as cocoa and sugar, when they ask for

chocolate powder. In fact, the beverage prepared from such a mixture is most palatable if good quality beans have been used, as it can be made to a thickness of "blanc mange," if required, due to the gelatinisation of the starch which the powder contains, and a feeling of repletion, valuable to the poorer classes, is experienced after the consumption of a cupful prepared with boiling water, which may not be the case when ordinary cocoa powders are used.

Epps's cocoa preparation is a good example of a carefully manufactured article with high food value, and its composition has been already given.* A good chocolate powder may be prepared from the following recipe, in which it is assumed that the cacao mass is prepared from fine quality beans.

Chocolate Powder.

Cacao mass	20 lbs.
Arrowroot (slightly baked) . .	20 „
Sugar	59½ „
Vanilla	½ lb.
	100 lbs.

Unfortunately, we more often meet with recipes described as "ordinary chocolate powder," and which are composed somewhat as follows :

"Ordinary" Chocolate Powder.

Cacao mass	15 lbs.
Potato starch	15 „
Shell powder	15 „
Sugar	55 „
	100 lbs.

* *Vide* Chapter XVI, Table XXVIII.

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We are confident, however, that though such recipes find their way into books on cocoa and chocolate, the powders prepared from them do not often appear on the market.

The addition of cocoa husk or shell powder to cocoa and chocolate preparations is, however, by no means uncommon, as the following extracts taken from the 'Times' (June 10th, 1910) will show:

"At West London, before Mr. Fordham, W. D.......... was summoned at the instance of the Fulham Borough Council for selling cocoa which contained 60 per cent. of powdered cocoa shells.

"There was also a summons against .... for selling at a shop in Fulham a sample of cocoa which contained 20 per cent. of cocoa shells."

The former case was adjourned, the Public Analyst for Fulham being reported as follows:

"The cocoa of commerce was made of the bean deprived of its shell. There was a certain amount of nourishment, no doubt, in the shell, but the fibrous nature of the shell rendered the article very unpleasant. He did not suggest that there was anything deleterious in the sample before the Court. The shell was used for cattle food and in the cheaper form of chocolates. There was no standard in this country for cocoa."

CHAPTER XVIII

MILK CHOCOLATES AND CHOCOLATE POWDERS—ANALYSES AND RECIPES—NUT CHOCOLATES

The popularity of milk chocolates, which probably synchronises with the introduction of Peter's milk chocolate to the public, is well deserved. Whilst it is admitted that the best milk are worthy of competing against the best plain chocolates, there are a large number of so-called milk chocolates on the market of a glutinous and coarse nature, which cannot compare in palatability with the coarsest of the plain variety.

Booth, in a paper before the Seventh International Congress of Applied Chemistry, recommended that milk chocolate should be legally standardised as a "preparation composed exclusively of roasted, shelled cocoa beans, sugar, and not less than 15 per cent. of the dry solids of full-cream milk, with or without a small quantity of harmless flavouring matter."

In the better brands of milk chocolate, both English and foreign, this standard is undoubtedly conformed with, but so much depends upon the fineness to which the preparation is ground that chemical analysis alone will not show the excellence of any particular brand.

Competition, however, is a wonderful leveller of quality, and seeing that this exists to a high degree among chocolate manufacturers, competing brands of a good price show great similarity in quality.

For the cheaper brands it is only necessary to refer to a later page, where recipes are given for "ordinary" milk chocolates, to realise that there are greater possibilities of addition of cheap varieties of, or substitutes for, the ingredients composing them than in the case of plain chocolates. Booth,* however, has been fortunate in his selections of samples for analysis, and in his valuable contribution to 'The Analyst' gives the following results:

Table XXIX.—*Analyses of some Milk Chocolates.*

	English.									
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Total fat	30·6	32·7	36·0	23·7	27·0	35·2	29·55	35·7	34·6	33·3
made up of—										
{ Milk fat	7·0	2·6	6·4	2·7	4·6	4·7	8·2	8·3	3·0	7·6
{ Cacao butter . . .	23·6	30·1	29·6	21·0	22·4	30·5	21·35	27·4	31·6	25·7
Milk sugar	9·2	3·8	8·2	6·5	7·3	8·9	10·0	11·1	5·0	10·4
Cane or beet sugar . .	45·0	46·5	38·0	52·6	32·4	41·2	44·4	39·1	54·3	38·4
Foreign starch . . .	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*
Cocoa shell	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*
Nitrogen	—	—	—	—	—	—	—	1·10	0·76	1·68

Table XXIX—*continued.*

	Swiss, German, Austrian and Belgian.									
	XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.
Total fat.	31·5	29·9	30·0	30·8	29·5	29·2	31·5	33·4	30·9	31·3
made up of—										
{ Milk fat	7·7	6·6	8·8	5·8	7·9	13·6	8·1	5·7	8·4	8·3
{ Cacao butter. . . .	23·8	23·3	21·2	25·0	21·6	15·6	23·4	27·7	22·5	23·0
Milk sugar	7·5	10·0	11·0	5·2	10·8	8·4	9·0	7·5	5·5	7·7
Cane or beet sugar. .	36·1	45·6	42·2	35·0	52·7	36·2	42·7	42·9	50·2	42·2
Foreign starch . . .	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*
Cocoa shell	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*	*Nil*
Nitrogen	—	—	—	—	—	—	1·28	1·30	1·10	—

* N. P. Booth, 'The Analyst,' 1909, xxxiv, 139.

It is not difficult to reconstruct these figures and to produce synthetically a recipe for them. Thus, taking the analysis of the milk chocolates as showing—

English samples.	Average. Per cent.	Maximum. Per cent.	Minimum. Per cent.
Milk fat	5·5	8·3	2·6
Cacao butter	26·3	31·6	21·0
Cane sugar	43·2	54·3	32·4

and—

Foreign samples.	Average. Per cent.	Maximum. Per cent.	Minimum. Per cent.
Milk fat	8·1	13·6	5.7
Cacao butter	22·7	27·7	15·6
Cane sugar	42·6	50·2	35·0

a recipe composed as follows will comply with the above analyses in the main particulars:

	Recipe.		Cacao butter.	Milk fat.	Cane sugar.
Cacao mass	9·0	yielding	4·5	—	—
Cacao butter	20·0	,,	20·0	—	—
Cane sugar	41·0	,,	—	—	41·0
Vanilline sugar	2·75	,,	—	—	2·0
Milk powder (full cream, 25 per cent. fat)	27·25	,,	—	6·81	—
	100·00		24·5	6·81	43·0

A recipe given by Zipperer is next shown:

Cacao mass	28
Cacao butter	12
Cane sugar	36
Milk powder	24
	100

and this, on analysis on the same basis as above, would

give approximately: milk fat 6 per cent., cacao butter 26 per cent., and cane sugar 36 per cent.

Laxa* has given some analyses of commercial milk chocolates worthy of reproduction here.

TABLE XXX.—*Analyses of some Milk Chocolates.*

		Moisture.	Total proteids.	Casein.	Other proteids.	Fat.	Lactose.	Sucrose.	Other non-nitrogenous bodies.	Ash.
1	Gala (Peter)	0·77	9·66	—	—	31·47	7·32	27·51	21·40	1·87
2	Delta (Peter)	0·54	9·86	5·16	4·70	10·11	8·02	48·25	20·89	2·32
3	Croquettes (Peter) . . .	1·79	9·15	3·86	5·29	31·91	7·42	39·42	8·37	1·96
4	Milka (Suchard) . . .	1·22	8·13	4·43	3·70	32·33	8·70	35·93	11·87	1·82
5	Croquettes (Cailleur) . .	2·26	10·94	4·36	6·58	31·12	7·84	33·68	11·88	2·28
6	Croquettes crêmant (Cailleur) .	0·99	6·89	0·67	6·22	31·37	2·24	33·14	23·86	1·51
7	Villards	1·00	6·83	4·46	2·37	33·12	8·00	45·22	4·28	1·55
8	Alpina (Sprüngli) . . .	0·72	9·73	3·10	6·63	33·11	8·76	37·25	8·47	1·96
9	Marsner	0·23	5·02	0·40	4·62	35·25	1·46	46·46	10·31	1·27
10	Rigi (Hartwig & Vogel) . .	2·03	6·98	1·43	5·55	33·67	9·14	38·87	7·82	1·49

These analyses by Laxa will not, however, stand very close investigation if recipes are to be prepared from them.

In the first place he assumes, from the estimation of lactose, that there is an undue amount of this sugar in samples 3, 4, 5, 8, 10, a condition which he explains is due to the addition of milk sugar during condensation of the milk. This we think to be improbable, both owing to the high price of milk sugar, as compared with sucrose or even milk powder, and to the fact that we are unable to see any advantage to be derived by such addition.

Further, assuming that the whole of the lactose found be due to that naturally present in milk solids containing 25 per cent. of fat and 38·5 per cent. of lactose, and that the remainder is pure roasted cacao mass and cacao butter (added), we obtain the following recipes synthesised from Laxa's analyses.

* O. Laxa, 'Zeitsch. Nahr. Genussm.,' 1904, vii, 471.

TABLE XXXI.—*Syntheses of Milk Chocolates from Table XXX.*

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Cacao powder (fat free) .	26·0	25·1	13·4	14·0	18·4	31·0	5·3	11·6	15·2	8·7
Sugar	27·5	48·3	39·4	35·9	33·4	33·1	45·2	37·3	46·5	38·9
Milk solids (or powder) .	20·0	21·9	20·2	23·7	21·4	6·1	21·8	23·9	4·0	25·0
Cacao butter (total) . .	26·5	4·7	27·0	26·4	26·8	29·8	27·7	27·2	34·3	27·4

These results have been obtained by calculating the total amount of milk powder that would naturally contain the lactose estimated plus 5 per cent. for the moisture content. If Laxa's supposition that lactose has been added during condensation of the milk be correct, the figures for milk powder in Table XXX will be high, and consequently the cacao powder estimated by difference will be correspondingly too low.

The cacao butter is estimated by subtracting from the total fat found that due to the milk powder, on the reasonable assumption that the fat content of the milk powder was 25 per cent.

If, therefore, the milk powder figures are too high, the cacao powder values will certainly be too low, and already, with the exception of 7 and 10, we find the figures for cacao to be considerably above those usually met with in commercial milk chocolates.

Moreover, it must be realised that if the amount of roasted nibs or cacao mass is to be calculated, the figures under cacao powder must be doubled at the expense of those for cacao butter, since the mass contains 50 per cent. of fat.

We have, therefore, the following results for the cacao mass present in these chocolates: (1) 52 per cent.; (2) must necessarily be a powder, since the total fat content is too low to allow for "moulding," and the cacao butter present is too small to be made to combine with all the

cacao powder to give the equivalent in "mass"—hence cocoa powder must have originally been employed; (3) 26·8 per cent.; (4) 28·0 per cent.; (5) 36·8 per cent.; (6) 62 per cent. (with a small deficiency of cacao butter); (7) 10·6 per cent. (with a large excess of cacao butter); (8) 23·2 per cent.; (9) 30·4 per cent; (10) 17·4 per cent. (with a large excess of cacao butter).

The improbability of these figures will be seen when compared against those obtained by Booth, already given on a previous page, and when it is realised that so large a proportion of cacao mass as shown by Laxa, to be present in the majority of the milk chocolates examined, would completely mask the softening and flavouring qualities of the milk.

"Ordinary" milk chocolates, like "ordinary" plain chocolates, is the designation under which recipes for inferior brands are described in books dealing with confectionery.

A good example of such a chocolate would be found as follows:

Cacao mass	10
Cacao shell powder	10
Potato starch	10
Sugar	40
Vanilline sugar	2
Cacao butter or substitute	10
Milk powder (skimmed or separated) . .	18
Colouring matter	to desired tint.
	100

The possible combinations of cheap substitute ingredients are endless, and it is fortunate that the chemist is in a position to detect the addition, especially in such cases as milk and other chocolates, which, being compound articles, are without legal standardisation, and are

consequently not studied from this standpoint by those controlling the conviction for fraud against the "Food and Drugs Act."

Milk Chocolate Powders.

The remarks made under "chocolate powders" in the previous chapter apply here, with the exception that milk powder is added.

The milk powder should be full-cream, and no other addition, such as of starch or shell powder, should be permitted.

A good recipe is as follows:

Cacao mass	19
Cane sugar	57
Vanilline sugar	1
Milk powder (full-cream)	23
	100

Too often, however, the milk powder will be from skimmed or separated milk, and mixtures of starch and shell powder will be found to be incorporated, with the result that an inferior article will be produced, which will prejudice the public against all such preparations.

Methods of Preparation.

Previous to the introduction of milk powder, which is of comparatively recent origin, all milk chocolate preparations were made from condensed milk. Owing to the 66 per cent. moisture which the condensed milk contains, it is found necessary to reduce the water content so as to be able to mix the milk into the chocolate.

This is accomplished either by drying the condensed milk mixed with sugar and starch into a stiff paste, which is rolled out thin and broken, or cacao powder freed from a large percentage of its fat is used in place of the starch.

Or again, the condensed milk can be boiled with the sugar to the "ball" (250° F. or 121° C.), and then mixed in with cacao mass in a heated iron "melangeur" till the whole is free from moisture.*

There are now, however, on the market various high-class brands of milk powder which are eminently suitable for the preparation of milk chocolates.

Milk powders should contain from 4 to 6 per cent. of moisture, which is easily driven off in the ordinary process of manufacture into chocolate by the various operations during which the chocolate paste is raised in temperature.

Preparation of Condensed Milk.

As the consumption of milk chocolate is very considerable, the firms with a large demand for the preparation often find it desirable to erect their own milk-condensing plant, both for the purpose of being independent of the market fluctuations in supply and price of the manufactured article, and from the convenience of being able to condense the pure milk to any required degree.

Moreover in Switzerland, the home of milk chocolates, pure fresh milk is condensed for the preparation of their speciality, and it is doubtless due to this fact that the Swiss milk chocolates hold the premier position in the public taste.

A condensing milk plant, obtained from Messrs. Baker and Sons, at the cost of £275, consists of a copper vacuum pan with vertical tinned boiling tubes, so as to obtain a rapid natural circulation and quick condensation at a low temperature.

The taste and quality of the resulting condensed milk is largely dependent upon the low temperature of evaporation, as the characteristic taste of boiled or sterilised milk

* An alternative method is to place the condensed milk in a heated "melangeur" and continue to work until the milk is reduced to a dry mass. Cacao mass, sugar, and cacao butter are then added and the whole refined to the required smoothness.

develops to a greater degree the nearer to the boiling-point the milk is heated. This not only spoils the flavour of the chocolate to which the milk is added, but prevents it from acquiring that delicious flavour of fresh milk which is so much appreciated in the best milk chocolates.

Through the courtesy of Mr. Edwin P. Carpenter, manager of Casein Ltd., I am able to describe the method of manufacture of "Trumilk," which is simply pure fresh full-cream milk reduced to powder form.

As soon as the milk is received from the farmers it is thoroughly cleansed of any impurities, that may have got into it through carelessness or inadvertence, by passing it through separators.

The next process is pasteurisation of the milk. It is then passed to the vacuum pan and reduced to 12 Beaumé, which equals specific gravity 1·088. The reason for taking part of the water out of the milk *in vacuo* is that a certain amount may be removed at less cost than by passing it through the hot chambers.

From the vacuum pan the milk is carried to the various drying chambers called units. Each unit has its separate chamber and pressure pump. The drying chamber is a tiled room about 9 ft. square, heated with hot air to a maximum temperature of 76·6° C., and into which the milk is sprayed through an aperture about $\frac{1}{10}$ millimetre in diameter or about the size of the point of a needle at 200 atmospheres pressure. This spray is enveloped in a current of hot air drawn from a battery of steam pipes encased in insulated boxes. An exhaust fan draws filtered cold air through the heated boxes and discharges it into the heated chamber.

The moment the fine particles of spray come into contact with the hot air the moisture is immediately absorbed and carried off, and the solids of the milk fall to the bottom of the boxes. To prevent loss of any milk with the

expelled moisture taken from it, the hot air passes through a series of light cloth filters, which detain the powder but allow the moist air to escape. A shaking motion frees the meshes of the filters from powder, which falls into a receptacle below.

The milk powder so produced is minutely fine and completely soluble in water, whilst the natural fat in the resulting solution in water is in a state of almost perfect emulsion similar to that of normal fresh milk. By the above process the albumen of the milk is retained in its normal form and the enzymes of the milk are not destroyed.

There is no doubt that milk powder produced by the spray process, correctly carried out, is vastly superior in solubility and flavour to that made by other systems, such as the Just-Hatmaker, which involve the heating of the milk to a minimum temperature of 100° C. in order to procure desiccation—a temperature sufficiently high to cook the albumen of the milk, destroy the enzymes, and partially caramelise the sugar.

There is no reason why the finest milk chocolate should not be prepared from full-cream milk powder, such as "Trumilk," which possesses the natural flavour so highly valued by the Swiss manufacturers, who condense their local milk supplies in order to obtain this result.

A remarkably uniform product is obtained by the "Trufood" process, and shows on analysis the following composition:

Moisture	1·5
Fat	26·6
Milk sugar, etc.	38·4
Proteins	27·6
Mineral matter	5·9
Total	100·0

Analyses made by the author of condensed milk and

milk powder prepared from pure fresh full-cream milk, suitable for the manufacture of milk chocolates, are given :

	Condensed milk.	Milk powder.
Moisture . . .	64·16 . .	2·50
Fat	10·92 . .	25·60
Proteins . . .	9·52 . .	27·20
Total solids . .	35·84 . .	97·50
Ash	2·10 . .	5·94

The preparation of the highest quality milk chocolates calls for special machinery, though good results may be obtained if the directions given below are carried out.

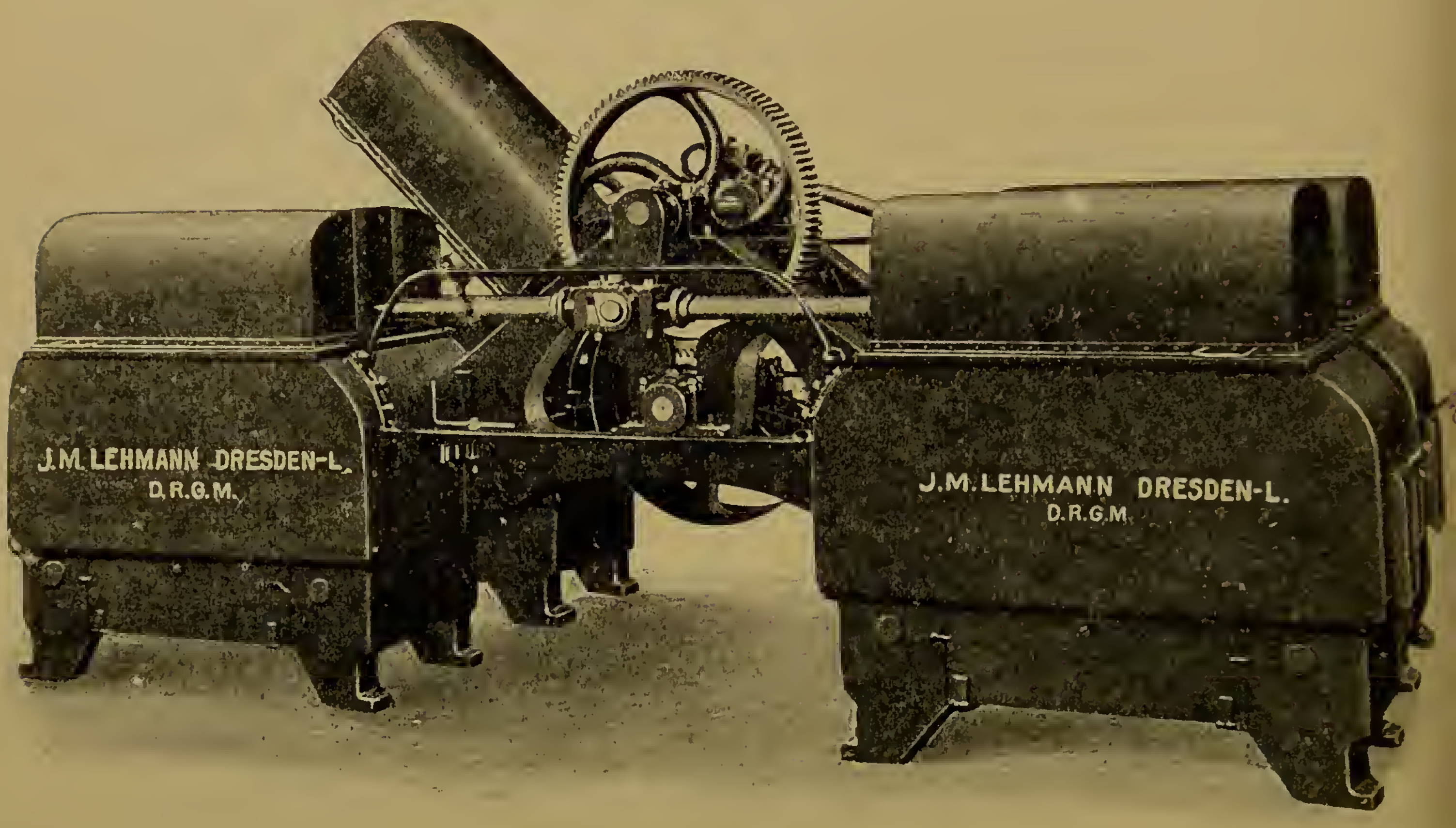
From condensed milk.—Mix the cacao mass or cocoa powder with the condensed milk, and work the finely powdered sugar in with the mixture. Roll the paste out thin and break up into small pieces, which should be placed in a drying stove at from 80°–90° C. When dry place in a "melangeur" and add sufficient melted cacao butter for convenient working. Refine five or six times with intervals of further kneading in the "melangeur" and rest in the hot cupboards, adding further quantities of cacao butter if necessary.*

From milk powder.—Thoroughly mix the cacao mass with the sugar and milk powder in a "melangeur" with sufficient melted cacao butter to render the whole easily workable, but reserving at least half the fat for subsequent addition. Refine once; the chocolate will now be very pale and in a fine powder. Replace in the "melangeur" with more cacao butter, and when thoroughly blended refine again. After the second refining place the paste in a pan in the hot cupboard and leave for several hours in order that the chocolate may attain a fatty consistency. Place again in a warm "melangeur" and then refine a third time. These operations should be repeated till the required smoothness and consistency are acquired.

* Or prepare as per footnote p. 170.

In moulding milk chocolate great care should be taken to wash the moulds frequently, as neglect of this precaution will cause the chocolate to stick. It might, with advantage, be pointed out that the moulds after washing should be *thoroughly* dried.

During the manufacture of milk chocolates an entirely different consistency of chocolate paste will be handled, the



By permission of Messrs. Bramigk & Co., London.

FIG. 14.—" Conche " machine for the preparation of " chocolat fondant " and Swiss milk chocolate. (See p. 175.)

presence of milk making a doughy mass, different from that of plain chocolates. Refining will have to be carried to a much further degree if milk powders are employed, as the powders are slightly granular and are difficult to break down. Insufficient refining will cause the chocolate, or rather the milk albuminoids which it contains, to agglutinate in the mouth, an unpleasant feature which may also be experienced if too much milk powder has been added.

The glutinous nature of milk chocolates and the

difficulty of reducing them to an even homogeneous consistency has led to the introduction of the so-called "conche" machine, which, by a system of pistons working into a receptacle containing the mass, reduces the chocolate to a mellowness extremely difficult to obtain by other processes without considerable expenditure of labour.

In the machine illustrated (Fig. 14) manufactured by Messrs. Lehmann, two or four tanks, each capable of holding a charge of 4 cwt., are attached. The interior of each tank is easily accessible for cleaning purposes, after the lid is raised, and as no working parts are situated above the tanks, dirt and oil are kept from contaminating the delicate and expensive chocolate material.

A four-tank machine of floor space of 13 ft. by $7\frac{1}{2}$ ft. and $5\frac{1}{4}$ ft. high costs about £260, and can be obtained from Messrs. Bramigk & Co.

Further uses for this machine are mentioned in the next chapter, when heating plain chocolate in order to produce a certain flavour due to the caramelisation of the sugar is considered.

Nut Chocolates.

Hazel nuts, almonds, and pine nuts are all used for producing chocolates of nutty flavour. In many countries and factories it is customary to include small quantities of nuts, either to produce a characteristic flavour or for softening the hardness of a plain chocolate.

The oil, which the nuts contain, lowers the melting-point of the cacao butter and can be detected by chemical analysis, as seen in a later chapter.

Special nut chocolates, frequently containing the whole nut of the hazel, almond, pine or even walnut, are to be found in confectionery shops under fancy names, which show that such additions have been made.

Large quantities of nut paste are often added to the

cacao mass and sugar in these cases, and where used it is certainly desirable that the nuts be roasted previously to being ground and added.

Even when the precaution of roasting has been made, maggots will frequently develop in nut chocolates, and considerable trouble between manufacturer and retailer may arise from this fact.

Besides killing the natural insect life which is present in 90 per cent. of nuts, especially in hazels, roasting enhances the flavour, and it is for this reason also that the process is to be recommended.

Analysis of nut chocolates will always reveal a higher percentage of fat than in the case of plain chocolates, as the nuts themselves contain from 30–40 per cent. of oil.

The addition of ground almonds, hazel nuts, pine nuts and walnuts will slightly lower the saponification value of the extracted fat, and will considerably raise the iodine value.

Butter fat, or the natural fat of milk, will raise the saponification value by a large amount, and will have little or no effect upon the iodine value.

The importance and estimation of these values will be considered in later chapters.

A good nut chocolate may be prepared from either of the following recipes:

	I.	II
Cacao mass . . .	28	17
Sugar	42	35
Roasted hazel nuts in paste.	27	40
Cacao butter . . .	3	8
Vanilla	to flavour	to flavour.
	100	100

The method of procedure for manufacture will be the same as for plain or milk chocolates already described, though some difficulty may be experienced in moulding, which should be conducted at the lowest possible temperature.

CHAPTER XIX

AROMA AND FLAVOUR DUE TO VARIETY OF BEAN, PROCESS OF MANUFACTURE, AND FLAVOURING MATERIALS, SUCH AS VANILLA, SPICES, ESSENCES, ETC.

The production of individual flavours in cocoas and chocolates is attained by—(1) selection of special variety or blend of cacao beans; (2) special process of manufacture; (3) addition of flavouring materials, such as vanilla, spices or essences.

Variety of Bean.

In Chapter VII the principal characteristics of the different varieties of cacao beans have bean dealt with, but the reader must have experienced the same difficulty in imagining, as the author had in detailing, the various flavours, which, though characteristic, are almost impossible of written description.

Venezuela, Ecuador, Guayaquil, Ceylon, certain West Indian and African beans may be said to be typical of the cacaos for producing the highest class chocolates, but even with these varieties blending is desirable, as less variation will occur in the flavour of a mixture of beans than in the individual kinds.

Caracas beans are strong and characteristic, Guayaquil Ariba slightly scented, Trinidad strong, bitter and pronounced, and Surinam similar to Caracas. All such cacaos

will require blending with those of less pronounced flavour if chocolate of fine quality is to be produced.

Those beans of bitter and harsh taste, such as certain of the Ecuador, Para, Bahia, Guiana, and Trinidad cacaos, will require toning up with beans of higher quality, while the cacaos of insipid or neutral flavour, such as those of Haiti and St. Domingo, will be improved by blending with beans of more pronounced character.

Further discussion on this subject is useless, for experiment with the different beans will be of more use to the manufacturer, who may require a certain flavour, than any description that it is possible to give.

Improvement in flavour may be brought about in beans of musty odour or great bitterness by treating them with water or alkali solution on arrival at the factory. The processes, which have already been described in Chapters IX and XII, consist of a "post" fermentation in the former case, and a modification of the bitter and astringent bodies in the beans by treatment with alkali in the latter. Besides improving the flavour it is claimed that these operations give better colour to the kernel and consequently to the chocolate prepared from them. If this be the case many of the lower grades of cacao that come into the market covered with mould, and of a pale interior, may be treated with advantage.

Process of Manufacture.

Treatment with alkali, temperature of roast, degree of fineness to which the chocolate is ground, period of working in the "melangeur," storage and packing of the finished chocolate, all play an important part in determining flavour.

It has already been pointed out that treatment with alkali is supposed by some to enhance the flavour of a cacao preparation, and whilst this may be so with a cocoa powder

which has the additional advantage of being rendered "soluble," it is not our experience that improvement is to be found in a chocolate so treated.

The presence of the small quantities of soda or potash which the treated chocolates contain is quite harmless, though there exists a certain prejudice against the use of chemicals in the production of food-stuffs.*

On the other hand, it is well known that even a small quantity of alkali in the presence of fat, especially when heat is applied, must produce a small quantity of soap or saponified fat.

Saponification of a fat, in all cases, seems to develop the pungent and unpleasant portion of the flavouring matter of that fat, and though it can be found stated by more than one authority that the addition of alkali prevents a fat from turning rancid, we are convinced that, unless very carefully and judiciously applied, the alkali will produce compounds of fat far more unpleasant to the palate than fatty acids, from rancid fat, present in the same proportion.

If, however, it can be proved that the addition of alkali neutralises the tannic acid and other acid astringent matters, and that the production of saponified fat is insignificant, then it must be admitted that a certain amount of good, apart from "solubility," has resulted by the treatment, for the bitterness and astringency of certain manufacturers' chocolates are serious hindrances to the full appreciation of their flavour.

The temperature of the roast determines whether the aroma of the beans has been fully, under-, or over-developed. When the cacao is fully roasted the beans have lost the acid, vinegary smell, and the nibs are free from any objectionable or musty odour which they may have acquired during the processes rendering them fit for market. Moreover, they have developed the pleasant aroma typical of

* *Vide* Discussion in Reports of Congress at Geneva and Paris, 1908, 1909.

chocolate, and which can best be judged away from the room in which the roast is taking place, preferably in the open air.

Under-roasted beans are most unpalatable when made up into chocolate, and can best be described by the word "green," signifying a flavour of raw vegetables.

Over-roasting, if unaccompanied by a smoky flavour, is not altogether unpleasant, and there is little doubt that the native and original Mexicans, who practised the art of chocolate making, roasted their beans to a higher degree than is now customary. The burnt flavour of over-roasted beans is considered by some to be pleasant to the palate, and certain "Mexican" chocolates of commerce are prepared from beans that have been severely roasted, or by the addition of small quantities of coffee berries to normal roasts.

Caramelisation of the sugar, already added to the roasted nibs, imparts a characteristic flavour to the finished chocolate.

This may be accomplished by heating the mixed chocolate paste in an iron "melangeur" from 115° C. to 120° C., extending over a period of time of thirty to forty-five minutes, so that the whole is gradually and evenly cooked. Care must be taken that no chocolate adheres for any length of time to the hot iron surface of the mixer, as a strong burnt flavour, of a most unpleasant nature, will result.

In such cases the beans should only be semi-roasted, as the subsequent cooking develops the half-acquired aroma of the cacao, while the cooking should be conducted before refining, as the very finely divided sugar and cacao mass are apt to over-burn.

The operation of caramelisation may with advantage be conducted in the "conche" machine already described under the heading "Milk Chocolate," as the receptacles are espe-

cially adapted for heating to high temperatures. The rise of temperature should be gradual and evenly distributed over the vessel containing the chocolate to be cooked.

Similar, but in our opinion inferior, results are obtained by preparing beforehand the caramelised sugar, *i. e.* sugar heated to 182° C., and adding it to the cacao mass in the "melangeur," or by carrying the processes suggested in Chapter XVII for the preparation of "soluble" cocoas and chocolates by the boiling of strong sugar solutions with cacao mass to a further degree, and until the flavour of caramel is obtained.

The roughness to the palate of the older-fashioned dry chocolates is due to the fact that the cacao mass and sugar are not refined to such an extent as the smooth "fondants" chocolates so popular at the present time. Close refining, while giving smoothness to chocolate, is apt to rob it of its aroma, especially if the finished article is allowed to lie about exposed to the air.

Chocolate, like flour and milk, readily takes up odours to which it is exposed, and it is consequently very necessary to prevent strong-smelling matters from coming into contact with the chocolate, and from tainting the atmosphere of the rooms in which chocolate is stored.

Chocolate should never be packed direct in cardboard or plain paper, as the stale flavour imparted is most unpleasant, but all tablets should be wrapped in tinfoil previous to packing. In sampling chocolate it will be found that tablets will have developed their aroma for better or for worse after two or three weeks; freshly moulded tablets never convey to the palate the true flavour of the chocolate.

Flavouring Materials, such as Spices, Essences, etc.

The principal flavouring materials added to cocoas and chocolates are vanilla, or its substitute, vanillin, cinnamon,

nutmeg, cloves, cardamoms, coriander, balsam of Peru, gum benzoin, almonds, hazel-nuts, praliné, pine-nuts, coffee and milk.

Of these by far the most popular flavour for plain eating chocolate is vanilla.

Vanilla and vanillin.—The vanilla of commerce is the seed pod of the parasitic orchid *Vanilla planifolia*, which is cultivated in Mexico, Tahiti, Mauritius, Mayotte, Java, Seychelles and Ceylon.

The fresh pods do not contain much of the aromatic bodies characteristic of the vanilla beans of commerce, but this is developed in the subsequent treatment of a fermentative character which the beans are caused to undergo.

Fine vanilla beans come into the market in tin boxes as long moist black pods, usually covered with an efflorescence of white crystals. These crystals are aromatic and volatile, and consist of vanillin and a certain proportion of benzoic acid.

During preparation it is necessary to dry the beans, as not only do they rapidly develop mould when moist, but in the dry state they better retain their aroma.

Inferior vanilla, from improper curing or from trees of other species of vanilla, bearing fruit of lower value, are frequently treated by rolling the pods in synthetic vanillin, benzoic acid, etc. For the detection of such fraud the chemical reactions of the possible adulterants should be investigated.

From Brazil is obtained the species called Vanillon, possessing a long bean of strong but less aromatic flavour.

Vanilla beans may be used either as "vanilla sugar," in which case the beans are cut up fine and mixed with sugar, and the whole reduced to a fine powder, or as extract, when an alcoholic solution is prepared by soaking the beans in the solvent.

Vanilla sugar.		Vanilla extract.	
Vanilla beans (fine ground) . .	1 part	Vanilla beans (fine ground) . .	4 parts
Sugar . . .	5 parts	Alcohol . .	5 ,,

The vanilla extract should be prepared by soaking the pods, finely crushed or ground, in alcohol for forty-eight hours, when the clear extract can be decanted or filtered off.

All vanilla preparations, as also all materials used for flavouring purposes, which owe their properties to volatile matters, should be kept in closely sealed vessels or bottles.

The objection to the use of "vanilla sugar" and other preparations of the vanilla pod in which the whole bean is used, is the presence of the black specks or seeds, which renders unsightly the sugar or any light-coloured material so flavoured. This objection does not hold good for cocoa and chocolate, which are flavoured to the best advantage with vanilla bean. From the financial point of view, the use of synthetic vanillin, which in recent years has almost entirely replaced the vanilla bean for cocoa and chocolate flavouring, is to be recommended.

Vanilla beans seldom contain more than 2·5 per cent. of vanillin, to which is principally due the aromatic property of vanilla. Vanillin was first synthesised in 1872 from oil of cloves, and the artificial product has steadily worked its way into the favour of the confectioner, both on account of its efficiency and low price per flavouring unit as compared with those of the natural bean.

The respective prices of vanilla beans and vanillin are at the present time 13*s*. and 12*s*. 6*d*. per pound.

Vanillin sugar.		Vanillin extract.	
Vanillin . .	1 part.	Vanillin . .	1 part.
Alcohol (hot) .	5 parts.	Alcohol (hot) .	5 parts.
Sugar . .	20 ,,		

Vanillin is not so readily soluble in cold as in hot

alcohol, consequently to accelerate solution hot alcohol is preferably mixed with the vanillin crystals. In the preparation of "vanillin sugar," the dry, fine sugar is rubbed with the solution, added very slowly, and when the whole is quite dry it should be tinned up immediately to prevent evaporation of the volatile aroma.

Vanillin has approximately forty times the flavouring power of vanilla, consequently, in the recipes given, both the "vanillin sugar" and extract will be stronger than the corresponding preparation from the natural bean. The amount of vanilla and vanillin used in the preparation of "sugar" and extract are, of course, optional, and can be varied to taste and requirements.

The flavour of the bean is undoubtedly superior to that of its synthetic substitute, less harsh and more delicately aromatic, but the advantages to be obtained by the use of the latter are so great that they will outweigh the superior flavouring properties of the former, except in cases where the most delicate palates are to be pleased.

The handling of vanilla beans and vanillin is attended with some inconvenience, as the aromatic bodies they contain are most pungent and irritating to the nostrils. Moreover, they set up irritation of the skin and cause sores, which, though not attended by danger, are extremely unpleasant and distressing.

Almonds, nuts, etc.—Hazel-nuts and almonds are used extensively on the Continent for giving a slight nutty taste, though when used in England much larger quantities of nut-paste are added, and the compound article is sold under some fancy name, such "Noisette," "Nut Chocolate," "Nuttis," etc. Whole roasted nuts are frequently embedded in the chocolate, and enable a harder chocolate, which still possesses the nutty characteristic, to be made.

When nut or almond paste is added to chocolate mass the melting-point of the mixture is considerably lowered

from that of plain chocolate, owing to the presence of oil which the nuts contain. Consequently a good nut chocolate is always softer than the ordinary plain variety, and is more difficult to handle in the factory. Cacao butter substitutes possessing "hardening" properties will frequently be found in the cheaper grades of nut chocolates.

The same remarks apply to milk chocolates, though the presence of the large proportion of casein tends to give body.

Soft chocolates of these varieties will not possess "snap," which is so characteristic of hard plain chocolate. "Snap" is due either to the presence of a large proportion of cacao butter, which itself possesses a hard, crisp break, or to the thorough blending and working of the sugar and cacao mass in the "melangeur" during manufacture. This property may also be acquired by rapidly cooling the chocolate after moulding.

The addition of oil, the presence of air-bubbles in moulded chocolate, and insufficient working, will all tend to the reduction of "snap."

Spices, etc.—The spices, cinnamon, nutmeg, cloves, cardamoms, and coriander, may be added direct to the chocolate paste in the "melangeur," though, owing to the gritty nature of ground spices, and to the fact that a certain amount of sand is always to be found in them, their essential oils are employed with advantage.

Another point in favour of using the essential oils in preference to the ground spices, is that a more constant and equal flavouring material can be prepared, as the natural spices fluctuate considerably in the potency of their aromatic contents.

It is not an uncommon occurrence to meet with ground spices on the market which have been partially deprived of their essential oils or mixed with starch, meal, etc., and spices so treated would naturally be of lower value for

flavouring. The characters of the spices are too well known to need description, and the quantity to be added to chocolate too much a matter of taste to justify a catalogue of recipes.

It is not intended, therefore, to more than outline the method of procedure for the preparation of spice flavourings.

If the powdered spices are used, it is advisable to wash, dry and grind the spices on the factory premises, as such a proceeding prevents any possibility of adulteration.

If the essential oils are employed, it is advisable, as with vanillin, to prepare an alcoholic solution, as, when the flavouring mixture is measured out, the errors, which will occur in the volumes of many consecutive measurements, will be of the less importance the greater the dilution.

This error might be considerable if the essential oil were used pure and undiluted; further, the advantages to be gained by making an alcoholic solution for the preparation of "cinnamon sugar" and "clove sugar," by the same method as "vanillin sugar," are such that less intimate mixing will be required, and less possibility of making serious error will result.

The addition of strong flavouring materials to a food preparation is one of those matters which, at present, must be left to the discretion of the human automaton, and if errors are to be prevented the processes must be rendered as "fool-proof" as possible, especially in a large factory.

A 10 per cent. alcoholic solution of an essential oil is a convenient dilution for working, and where used *per se* should be added to the chocolate at as late a stage of its manufacture as possible, to ensure that the least amount of volatile flavouring matter escapes.

There are many chocolate improvers on the market at the present day, but all those that have come under our notice have been prepared from essential oils of spices, extract of cacao shells or coffee, or blends of them.

Gum benzoin, etc.—Balsam of Peru and gum benzoin, both being soluble in alcohol, are used in solution. The balsam derives its flavour chiefly from the esters of benzoic and cinnamic acids, and, owing to its strong and burning taste, must be judiciously added to chocolate, which may be greatly improved by the presence of a small quantity.

Gum benzoin in 25 per cent. alcoholic solution is principally used for chocolate varnish, the highly shining surface of decorative chocolate work or exhibition chocolate, that is required to maintain its lustre while exposed, being obtained by this means.

Coffee.—The addition of roasted coffee to chocolate gives a very fine flavour, and if used in extremely small quantities is difficult to detect as the flavouring material.

The coffee should be added to the chocolate mass running in the "melangeur" for the first time, as the hard and gritty nature of the ground and roasted coffee makes it desirable that it should be refined at least as often as the chocolate. Three parts of ground and roasted coffee to one hundred parts of chocolate mass is a good proportion, though to increase the flavour as much as 5 per cent. of coffee may be used. Higher than 5 per cent., the colour of the chocolate will suffer, and the grittiness due to the coffee may be felt.

The trouble of grittiness may be overcome by steeping the coffee-grains, contained in a muslin bag, in melted cacao butter, which extracts all the aromatic oil. This, however, cannot be recommended as an economical method, seeing that little or no "return" in weight is obtained.

Coffee extracts may also be used, and if prepared fresh from freshly roasted and ground coffee will give good results.

PART III

CHEMISTRY OF CACAO

CHAPTER XX

SURVEY OF THE COMPONENT PARTS OF ROASTED CACAO BEANS—HUSK

Roasted cacao is divided up during the process of manufacture of cocoa and chocolate into—(1) the husks or shells, which are the by-product and of little value; (2) the nibs, which, as has been seen in the foregoing chapters, should comprise the base for sweet and fancy chocolates, and which, when partially deprived of fat for cocoa powders, constitute the most commercially important fraction of cacao.

Husk (12 per cent. to 20 per cent. of the whole bean).

König has shown the amount of husk determined by Laube and Aldendorff to vary considerably with the origin of the bean. This is not remarkable when the different processes which the beans undergo in fermenting and curing in various localities, and previously described in Chapter VIII, are considered. The following table (Table XXXII) shows two sets of results obtained by different authors on various cacaos.

The considerable variations which occur between the figures of different observers is attributable to the varying proportions of sand and earth adhering to the beans. Such differences frequently occur between the figures of the same variety of bean sold under the same mark.

TABLE XXXII.—*Percentage of Husk in Cacao Beans.**

	I.	II.
Caracas	20·09	15·00
Guayaquil	—	18·68
Trinidad	14·04	14·68
Puerto Cabello	14·92	12·28
Soconusco	18·58	—
Surinam	—	14·60
Machala	—	16·14
Port au Prince	—	16·00

I. König, 'Die mensch. Nahr u. Genussm.,' i, 261.
II. Zipperer, 'Untersuchungen über Cacao, etc.,' 55.

The chemical composition of husks from cacao of different varieties is embodied in Table XXXIII.

TABLE XXXIII.—*Composition of Husk.*†

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Water	12·57	5·12	—	—	9·30	12·51	4·50	7·83
Fat	3·30	12·92	3·6	—	3·83	4·23	4·40	6·38
Ash	7·35	6·92	5·7	6·46	8·26	10·20	7·30	7·12
Nitrogen	—	2·63	2·05	—	3·00	2·19	2·50	—
Proteid	14·69	16·44	12·8	—	18·81	13·69	—	14·29
Fibre	16·33	13·17	—	13·05	13·85	16·71	14·00	14·69
Theobromine, caffeine	0·79	—	0·58	—	—	—	—	—

I. G. Paris, 'Zeitsch. Nahr. Genussm.,' 1898, vi, 389.
II. F. T. Schutt, 'Annual Rep. Exptl. Farms (Canada),' 1898, 151; 1899, 851.
III. S. Dekker, 'Chem. Centr.,' 1902, ii, 1217.
IV. H. Luhrig, 'Zeitsch. Nahr Genussm.,' 1905, ix, 263.
V. A. Smetham, 'Jour. Royal Lancs. Agric. Soc.,' 1909.
VI. Zipperer, 'Untersuchungen über Cacao, etc.,' 55.
VII. N. P. Booth, 'The Analyst,' 1909, xxxiv, 144.
VIII. König, 'Die mensch. Nahr Genussm.,' i, 261.

Besides these analyses there are many other contributors to our existing knowledge of the component parts of cacao husk. The researches of Matthes‡ and his co-workers are

* *Vide* also Chapter VII and Chapter XI, Tables XVIII and XIX.
† *Vide* also Chapter X, Table XIII.
‡ Matthes, etc., 'Ber.,' 1907, xv, 4195, and 'Zeitsch. Nahr Genussm.,' 1906, xii, 159, etc.

worthy of comment, as also are those of Filsinger* and Welmans.†

In the foregoing table Luhrig's figures are calculated on the dry substance. Paris', Schutt's and Smetham's results were obtained in ascertaining the food value of cacao husk, a waste product of the chocolate factory, for cattle food. The utilisation of the husk for the preparation of a marketable product would be of great value to the cocoa and chocolate manufacturer, and the subject has occupied the attention of many chemists, agriculturists and others.

The introduction of cheap oil-cakes has somewhat limited the possibilities of using cacao husk for cattle food. Some excellent results have been obtained, however, with cacao husk cake on experimental farms. The feeding of cattle, milch cows, etc., on cacao husk, made up in a similar way to the modern oil-cakes, has shown that the animals thrive on the diet and put on weight. The amount of cream yielded by the milk of cows fed on cacao cake was found to be larger than from grass-fed animals, and after a prolonged treatment the quantity of milk per cow was noted to sensibly increase also.

The results of experiments can be found in the records of the Society of German Chocolate Makers,‡ the annual reports of experimental farms in Canada, and other works where the subject-matter deals with the valuation of waste cacao products, cattle food stuffs, manures, etc.

Other uses to which cacao husk has been put are for extraction of the fat, preparation of a colouring material, extraction of theobromine, as soil manure, preparation of a flavour for adding to roasted coffee and its substitutes, or to cheap and inferior cocoa powders and chocolate.

At the present day, with modern efficient machinery,

* Filsinger, 'Zeitsch. öffent. Chem.,' 1899, etc.

† P. Welmans, *ibid.*, 1901, vii, 491.

‡ 'Korr, Verband. Deutsch. Schokoladefab,' 1896, 32.

very little cacao nib dust finds its way into the waste shell receptacle during the process of nibbing, winnowing, and grading, consequently the percentage of fat, which commercial cacao husk contains, is due, almost entirely, to that present in the shell alone.

The fat content in cacao husk ranges from 3 per cent. to 6 per cent., and practically all this is capable of extraction by a suitable solvent such as petroleum ether. The fat so extracted is low in quality and would be rejected for use in better-class chocolate factories; it does, however, find a market, and might with advantage be used in the preparation of cosmetics, etc., in which flavour is of less importance.

After the fat has been removed, the residue may be treated with sulphuric acid (3 per cent. solution), boiled, neutralised with baryta and extracted with chloroform, which removes the caffeine and theobromine, of which the husks contain some 0·6 per cent. Dekker obtained 0·58 per cent. of mixed alkaloids by treatment of the husks with magnesia, boiling with water and extracting with chloroform. The separation of theobromine and caffeine may be accomplished by a further extraction with carbon tetrachloride or cautious treatment with caustic soda. In the first case caffeine is soluble in carbon tetrachloride; in the latter theobromine is removed, without the caffeine, by the soda.

The husk finds further outlet in chocolate surrogate, or "suppen powder," which consists of a small quantity of cacao waste, and sugar, meal, spices and colouring matter in varying quantities. This constitutes a cheap chocolate powder of very inferior quality.

A cacao shell powder of commerce analysed by the author showed 9·8 per cent. moisture, 7·2 per cent. ash, 10·2 per cent. fat, 15·6 per cent. albuminoids or proteid matter. Such a powder shows a good value on analysis, but the remaining 57·2 parts is of an indigestible fibrous

nature which might reasonably set up irritation in a weak stomach.

"Cocoa tea" of Germany and "miserables" of Ireland are independent articles of commerce, and consist of cacao husks, in powder or shred, the infusion of which in boiling water is drunk after the manner of tea by the poorer classes of the two countries.

An infusion of cacao husk is not unpalatable, and when concentrated is used for improving the flavour of cheap cocoas. The preparation of "improvers" from cacao husk forms the subject of many English, French, and German patents.

The composition of cacao husk from beans of different origin does not show important variations; such differences as do occur are attributable to the varying proportions of earth, sand, and similar extraneous matter found adhering to the outer shell, and to the percentage of moisture which, owing to the different processes of curing and drying undergone, shows considerable variation.

Booth* has shown some interesting figures which are worthy of reproduction, since they provide information on the alkalinity and cold water extract, the results for the latter being of importance in the estimation of the cacao present in a sample of cocoa or chocolate.†

TABLE XXXIV.—*Analyses of Roasted Cacao Husk.*

	Ceylon.	African.	Para.	Guayaquil	Puerto Cabello.
Total mineral matter	6·61	5·63	6·78	8·19	20·82
Soluble mineral matter	4·78	3·53	4·39	5·25	5·24
Siliceous matter	1·00	1·79	0·72	1·45	8·33
Alkalinity as K_2O	2·54	2·63	2·80	3·36	1·13
Cold water extract	20·70	20·40	18 70	24·60	23·50
Nitrogen	2·40	2·91	—	2·13	—
Fat	3·10	3·50	—	5·90	5·68
Fibre	12·80	15·70	—	12·85	13·83

* N. P. Booth, 'The Analyst,' 1909, xxxiv. 144.

† *Vide* Chapter XXVI.

The average moisture of the shells was 4·5 per cent. against 3·0 per cent. for the average of the corresponding nibs, while the "cold water extract" was found to be the same for all practical purposes in both nib and shell.

The composition of cacao husk having been now dealt with in the general way, there remains the important consideration of the individual components, which will be taken *seriatim*.

MOISTURE (5 per cent. to 12 per cent. of the raw, 2 per cent. to 8 per cent. of the roasted husk).

The amount of moisture which any given sample of cacao husk will contain will depend, firstly, upon the degree to which the particular beans were dried; secondly, to the treatment which they may have suffered during transit or storage; and thirdly, upon the degree of roasting, and the time of standing before the sample was taken.

There is little need for further discussion on this point, as figures illustrating the percentage content of moisture in beans fresh from the pod, after fermentation, raw commercial, before and after roasting, will be found in this and preceding chapters.

FAT (3·5 per cent. to 8 per cent. of the raw, 4 per cent. to 10 per cent. of the roasted husk).

The fat which is present in the husk is the same as that found in the kernel, and is commercially known as "cacao butter," or "cocoa butter," though the latter term should not be used, as confusion will arise between this fat and that obtained from the coconut palm (*Cocos nucifera*).

There is an extremely small proportion of fat in the original fresh husk of the cacao bean, the quantity found in the fermented and dried bean being chiefly due to that absorbed from the kernel.

Cacao fat is a mixture of glycerides of fatty acids, and contains, besides stearin, palmitin, olein, and laurin, the glyceride of arachidic acid. The occurrence of theobromic acid ($C_{64}H_{128}O_2$) has been mentioned by Kinzett,* but disputed by both Graf † and Traub,‡ who were unable to find any fatty acids of higher molecular weight than arachidic.

A very large number of investigators have studied the composition of cacao butter. Hehner and Mitchell § found 40 per cent. of stearic acid; Farnsteiner‖ obtained 59·7 per cent. of saturated acids, 31·2 per cent. of oleic acid, and 6·3 per cent. of other acids. Klimont,¶ who regards these acids to exist mainly in the form of mixed esters, has isolated the following substances by fractional crystallisation of the fat from acetone:

(1) A fraction melting at 70° C., and having an iodine value = 0. This he regarded as a mixture of tripalmitin and tristearin.

(2) A fraction melting at 31° to 32° C., with a saponification value = 196·4, iodine value = 28·9. This fraction had an empirical formula ($C_{55}H_{104}O_6$), and was judged to be a mixed triglyceride, oleo-palmito-stearin.

(3) A fraction melting at 26° to 27° C., and having an iodine value = 31·7, a saponification value = 210, and an empirical formula ($C_{51}H_{96}O_6$). This Klimont considered to be a mixed glyceride, containing the radicles of myristic, palmitic and oleic acids, and possibly of some still lower fatty acids. Triolein was not detected in the fat.

Matthes and Rohdlich,** in determining whether cacao

* C. Kinzett, 'Journ. Chem. Soc.,' Trans. 1878, xxxiii, 38.

† Graf, 'Arch. Pharm.' (3), xxvi, 830.

‡ Traub, *ibid.* (3), xxi, 19.

§ Hehner and Mitchell, 'The Analyst,' 1896, xxxi, 321.

‖ Farnsteiner, 'Zeitsch. Nahr Genussm.,' 1899, ii, 1.

¶ Klimont, 'Monatsch.,' 1902, xxiii, 51; 1905, xxvi, 563; 'Ber. Chem. Ges.,' 1901, xxxiv, 2636.

** Matthes and Rohdlich, 'Ber.,' 1908, xli, 19.

butter contained any constituent with a pronounced influence upon the flavour of cacao, succeeded in isolating from the unsaponifiable matter two phytosterols identical apparently with sitosterol and stigmasterol previously isolated by Windhaus from the fat of the calabar bean. There was also present an oil with a pleasant smell, resembling hyacinth. Fritzweiter* isolated 6 per cent. of oleodistearin from the fat which had been removed by Heise's method.

Other contributors to our existing knowledge of the composition of cacao butter that must be mentioned are Lewkowitsch,† Strohl,‡ De Negri and Fabris,§ Filsinger,‖ Wright,¶ Rakusin,** etc., whose works should be consulted if further information is required.

According to Schädler, cacao butter has the following elementary composition: Carbon 75·20 per cent., hydrogen 11·90 per cent., oxygen 12·90 per cent.

Cacao butter is a yellowish solid, turning gradually white on keeping. It breaks with a smooth fracture, and possesses an odour resembling that of cacao, and a smooth and pleasant taste. The fat softens at 26·6° C., and melts between 31·1° and 33·9° C.

The British Pharmacopœia test for its purity is as follows: If 1 gr. be dissolved in 3 c.c. of ether, in a test-tube at 17° C., and the tube placed in water at 0° C., the liquid should neither become turbid nor deposit a granular mass in less than three minutes; and if the mixture, after congealing, be exposed to a temperature of 15·5° C., it should gradually afford a clear solution (absence of

* R. Fritzweiter, 'Chem. Centr.,' 1902, i, 1113.

† Lewkowitsch, 'Journ. Soc. Chem. Ind.,' 1898, xviii, 556, etc.

‡ A. Strohl, 'Zeitsch. anal. Chem.,' 1896, xxxv, 166, etc.

§ De Negri and Fabris, 'Ann. Lab. Chim. Centr. delle Gabelli,' 1891, xcii, 258, etc.

‖ Filsinger, 'Zeitsch. anal. Chem.,' 1896, xxxv, 517, etc.

¶ Alder Wright, 'Oils, Fats and Waxes, and their Manufactured Products,' 1903, 529, etc.

** M. Rakusin, 'Chem. Zeit.,' 1905, xxix, 139, etc.

other fats). This is a modification of Björklund's ether test.*

The physical and chemical constants of cacao butter have been estimated by a number of investigators, and will be found classified in Table XXXVI. It is, however, desirable to discuss the meaning of these constants in order to understand their significance.

The Specific Gravity.

The specific gravity, or the " weight of unit volume " of the fat, compared with that of water at the same temperature, is extremely useful in determining the purity or nature of the fat under consideration. In the case of cacao butter this is especially so, as its specific gravity in the solid state is higher than the fats with which it is likely to be confounded or adulterated, whilst in the liquid and molten state the specific gravity will be found to be lower than its probable adulterants (*vide* Table LIV.).

In taking the specific gravity of the solid fat it is necessary to allow the oil to remain solidified for several days in order to assume its normal crystalline form.

It has, moreover, been shown by a number of observers that an expressed fat has a different specific gravity to an extracted fat; it is therefore necessary when taking the value to state by which process the fat has been obtained, and to also state the age of the sample. Thus Hager gives the normal specific gravity of cacao butter at 15° C. as 0·95 when fresh and 0·945 when old. Later values by the same investigator for fresh butter are from 0·96 to 0·98 at 15° C. Cacao butter extracted by solvents shows a higher specific gravity than the expressed fat, Rammsberger finding values of 0·85 for expressed and 0·99 for extracted fat.

* *Vide* Chapter XXIV.

The Melting-point.

The melting-point of cacao butter is usually given as 33° C., but figures ranging from 28° C. to 36° C. are to be found recorded by various investigators. The differences found may usually be attributed to a different source of origin. The melting-point of cacao butter extracted from beans of various cacaos has been frequently shown to vary; thus White and Braithwaite and others give the following results:

TABLE XXXV.—*Variation of Melting-point of Cacao Butter, with Source of Origin.*

Bean.	Melting point.		
	I.	II.	III.
Guayaquil Machala	34·0	33·75	—
Caracas	34·0	33·30	—
Guayaquil Ariba	31·5	—	—
Port au Prince	33·8	—	—
Puerto Cabello	33·0	—	—
Surinam	34·0	—	—
Trinidad	34·0	32·00	—
Grenada	—	33·15	—
Ceylon	—	34·05	—
Kauka	—	—	32·25
Bahia	—	—	33·05
Porto Plata	—	—	33·35

I. Zipperer, 'The Manufacture of Chocolate,' 1902, 39.
II. White and Braithwaite, 'Brit. and Col. Druggist,' 1897, xxi.
III. 'Korr. Verband. Deutsch. Schokoladefab,' 1889, v, 65.

Old butter has, moreover, a higher melting-point than fresh extracted or expressed fat.

De Negri and Fabris give the melting-point of cacao butter as 28° C. to 30° C., and the solidifying point as 21·5° C. to 23° C.

The determination of the melting-point by itself is no criterion of the purity of the cacao butter.

The Bromine and Iodine Absorption Values.

Organic compounds containing a group of the character CR=CS tend to combine under suitable conditions with members of the halogen group such as iodine and bromine.

By determining the amount of halogen fixed by a given acid or mixture of acids, useful information as to the nature of the fatty acids present is obtained. Thus in a simple case:

$$\underset{\text{Oleic acid.}}{C_{17}H_{33}CO.OH} + Br_2 \rightarrow \underset{\text{Dibromostearic acid.}}{C_{17}H_{33}Br_2.CO.OH.}$$

In determining the halogen absorption value, it is simpler to make use of the iodine method, and it is intended here to consider only this quantity, the bromine equivalent being easily found in works treating with oils, fats, etc., or calculated from the iodine figures.

Stearic acid does not absorb iodine, whilst oleic acid takes up 90 per cent. of its weight of the halogen. We have, then, a means of partially discriminating between fats containing varying quantities of olein to stearin. Thus, to take extreme cases, the iodine value for cacao butter is about 35, while that for almond oil is about 100, and that of coconut stearin around 4.

Lewkowitsch has shown that the iodine value of cacao butter increases slightly with age, though still not outside the possibilities for normal fat.

The lowest value for iodine absorption of cacao butter that can be found is 32·0 by Dietrich, and the highest 41·7 by Strohl, though again neither values are much beyond the normal figures of Lewkowitsch, 34·27 to 36·99. Filsinger found that cacao butter from different varieties of beans showed varying figures of iodine absorption, ranging from 35·1 for Porto Plata to 37·1 for Guayaquil Ariba.

The iodine value indicates the amount of iodine per cent. absorbed by the fat, and is consequently a rough

indication of the unsaturated fatty acids of the oleic acid type present. The unsaturated fatty acids directly combine with iodine and bromine to form dibromo- or diiodo-substitution derivatives. The corresponding glyceride derivatives of the unsaturated fatty acids behave in like manner, thus:

$C_3H_5(C_{18}H_{33}O_2)_3$ +	$3I_2$	$\rightarrow C_3H_5(C_{18}H_{33}I_2O_2)_3$
Olein (glyceride of oleic acid)	Iodine	Glyceride of diiodo-stearic acid.

The method of bringing about this reaction is discussed in a later chapter, and is a very useful indication as to the purity of the fat under examination.

"Shell butter," or "Dutch ha" cacao butter, has, according to Filsinger, an iodine absorption value of from 39 to 40, and is, as a rule, higher than that of the fat extracted from the nib.

The Saponification or Koettstorfer Value.

The saponification value consists in determination of the number of milligrammes of potassium hydroxide required to saponify 1 grm. of the substance. The various glycerides, of which most of the fats are composed, are constituted so that, on saponification, they break up into glycerol or glycerine and the alkaline salt of the fatty acid they contain. Owing to the different molecular weights of the various fatty acids, the quantity of alkali that will be required to bring about saponification will vary. The quantity of potassium hydroxide requisite for complete saponification of a fat or glyceride is therefore a measure of the molecular weight of the fatty glyceride or mixture under consideration, and represents not only the free but the total fatty acids present.

The saponification value of cacao butter ranges from 192 to 202 (Filsinger) and is usually 194 to 195. The figures obtained by various investigators vary very little,

even the ageing of the fat causing but small increase, which is easily understood when it is realised that the saponification value is a measure of the total fatty acids present which would not be increased by the fat becoming rancid.

Acid Value.

The hydrolysis or breaking down of the fats into simpler forms, of which the fatty acids form the principal part, occurs to a small extent on the extraction of the fat by means of solvents or expression, and always takes place to a greater or lesser degree after detaching the fat-containing seeds from the plant.

This is brought about by the hydrolytic enzymes and ferments of the vegetable kingdom, whose duty it is to break down the fat to form readily assimilable food for the growing plant.

The presence of free fatty acids in any quantity is most detrimental to the flavour of the fat, with the exception of olive oil, whose flavour is supposed to be improved by a small quantity of fatty acids.

In cacao butter, which is not liable to turn rancid, the presence of fatty acids is most objectionable, and it is very easy to recognise a tainted sample.

Lewkowitsch* has determined the acid value of a number of samples of cacao butter, and whilst the ordinary fresh fat shows from 1 to 2 for a measure of free fatty acid, a sample kept for ten years in a sealed bottle had risen to 4·6. The maximum amount of fatty acids is found in fats extracted by solvents, and from beans which have been stored for a considerable time, as in these cases the fat has been in contact with the active ferments for the greatest period.

Rancidity or acidity is produced by the action of the

* J. Lewkowitsch, 'Journ. Soc. Chem. Ind.,' 1899, 556.

ferments in the presence of oxygen, and is greatly accelerated by exposure to light.

Ballantyne,* however, was unable to trace any connection between rancidity and liberation of fatty acids, though Spaeth† admitted that in the case of lard rancidity was attended by a considerable formation of volatile acids.

Rancidity is an oxidation process, brought about by the action of oxygen, light and ferments, and Spaeth observed that as the oxidation increased the power of absorbing iodine correspondingly decreased. Fats thus oxidised were observed to possess a considerably higher refractive index than the normal fats, which has been attributed to the polymerisation of the unsaturated fatty acids.

These facts are confirmed by Mjoen,‡ though he was unable to trace the action of bacteria or moulds in the process of oxidation.

The estimation of the chemical and physical constants of the fatty acids, in a similar manner to those of the fats, often affords valuable information as to the nature and purity of the fat under consideration.

The Reichert-Meissl Value.

The importance of the Reichert-Meissl value depends upon the fact that various natural oils and fats yield, on saponification, the alkali salts of fatty acids, many of which are volatile in steam. Their estimation constitutes this value.

In the case of butter from cow's milk the Reichert-Meissl value ranges from 25 to 33, whilst cacao butter never exceeds 1. Lewkowitsch found this value to be

* Ballantyne, 'Journ. Soc. Chem. Ind.,' 1891, x, 29.
† Spaeth, 'Zeitsch. anal. Chem.,' 1896, xxxv, 471.
‡ Mjoen, 'Forsch. Ber.,' 1897, iv, 195.

the lowest in a cacao butter kept for ten years in a sealed bottle, and records a figure 0·2.

The actual method of determining these figures will be found in a later chapter.

Refractive Index.

The power of refracting light, possessed by different oils, constitutes a valuable means of discriminating one from another.

Suitable instruments have been devised for determining refractive indices, the Zeiss butyro-refractometer, which is now so extensively used, being perhaps the most convenient form.

The refractive index of cacao butter has been recorded by Strohl as 1·4565 to 1·4578 at 40° C., and by Procter as 1·45 at 60° C. These figures represent roughly 46° to 48° on the Zeiss butyro-refractometer scale at 40° C.

TABLE XXXVI.—*Chemical and Physical Constants of Cacao Butter.**

	I.	II.	III.	IV.	V.	VI.
Specific gravity	0·964–0·974 at 15° C.; 0·8577 at 98° C.	—	—	—	0·964–0·974 at 15° C.	—
Melting-point .	30°–34° C.	26·6°–33°C.	29°–35° C.	32°–33·6°C.	30°–34° C.	30°–34·5° C.
Iodine value .	32·0–42·0	34·27–36·99	32·0–37·0	33·4–37·5	32·0–37·7	34·0–37·5
Saponification value . .	192·0–195·0	191·8–194·5	193·0–205·0	195·0	—	192·0–202·0
Acid value .	—	1·1–4·6	—	—	1·0–2·3	9·24–17·9
Reichert-Meissl value . .	0·2–0·9	0·38–0·94	—	—	—	—
Refractive index	—	—	Zeiss butyro-refractometer value at 40° C. 46–48°	—	—	Zeiss butyro-refractometer value at 40° C. 46–47·8°
Acetyl value .	—	2·71–2·86	—	—	—	—

The melting-point of the fatty acids obtained from cacao butter has been recorded by various investigators as from 47°–49° C. The author has examined

* For experimenters see over page.

one sample which melted at 52° C. The iodine value of the fatty acids has been found to be 39·0 (De Negri and Fabris).

I. Allen's 'Commercial Organic Chemistry,' 1910, vol. ii, 71.
II. Lewkowitsch, 'Journ. Soc. Chem. Ind.,' 1899, 556; 'Chemical Technology and Analysis of Oils, Fats, and Waxes,' 1909, etc.
III. Whymper, 1910.
IV. Filsinger, 'Korr. Verband. Deutsch. Schokoladefab,' 1889, v, 65; 'Zeitsch. anal. Chem.,' 1896, xxxv, 166, etc.
V. Dieterich, in R. Benedikt's 'Analysis of Fats and Waxes,' etc.
VI. Zipperer, 'The Manufacture of Chocolate,' 1902, 45.

Fibre (12 per cent. to 15 per cent. of the raw, 13 per cent. to 17 per cent. of the roasted husk).

The estimation of fibre in a cocoa powder or chocolate is a guide to the amount of cacao husk present. Ludwig* has made a series of analyses of known mixtures of husk and cacao, and, by estimating the amount of fibre (by a modified König's method†) in the samples, has given valuable assistance to the analyst desirous of ascertaining the extent of intentional or careless inclusion of cacao husk.

Six samples of cocoa powder gave 4·98 per cent. to 5·96 per cent. (average 5·60 per cent.) of crude fibre calculated on fat-free material; the quantity of fat present in the samples ranged from 25·05 per cent. to 27·92 per cent., giving an average of 25·78 per cent.

The sample of cocoa husk contained 3·08 per cent. of fat and 14·47 per cent. of crude fibre.

A mixture of equal parts of the six cocoas was then made, to which increasing proportions of husk were added with the following results :

* Ludwig, 'The Analyst,' 1906, 362.
† *Vide* Chapter XXV.

TABLE XXXVII.—*Crude Fibre in known mixtures of Cocoa and Husk.*

	Fat.	Crude fibre found.	Crude fibre calculated on fat-free cocoa.
Cocoa	25·78	5·50	5·60
„ + 5 % husk	24·37	6·03	6·16
„ + 10% „	24·00	6·39	6·71
„ + 20% „	21·44	8·06	7·79
„ + 40% „	16·62	10·18	9·74
„ + 60% „	12·04	11·72	11·48
„ + 80% „	8·26	13·28	13·04

The estimation of pentosans in cacao shells has occupied the attention of many observers.

The name of "pentose" is given to that class of hydrocarbon in which the alcoholic is joined to the aldehydic function, and their general formula is $C_5H_{10}O_5$.

The pentoses, like the hexoses or cane-sugar group, may be found almost everywhere in nature, the gums, arabic gum, cherry-tree gum, etc., being almost entirely composed of pentosans.

R. Adan,* who has carefully estimated the pentosan content of cacao husk, has shown it to contain 7·57 per cent. to 10·53 per cent. of pentosans, as against 1·19 per cent. to 2·19 per cent. for the nibs. P. Welmans† has given 8·5 per cent. for the husk and 2 per cent. for pure Dutch cocoa as the pentosan content, whilst Dekker‡ has published figures ranging from 8·18 per cent. to 9·63 per cent. for the husk, 2·17 per cent. to 2·41 per cent. for the nibs, and 2·56 per cent. for pure Dutch cocoa. Adan§ recently gave some results at the Seventh International Congress of Applied Chemistry held in London, which showed the variations of pentosan

* R. Adan, 'Bull. Soc. Chim. Belg.,' 1907, xxi, 211.

† P. Welmans, 'Zeitsch. öffent. Chem.,' 1901, vii, 491.

‡ S. Dekker, 'Chem. Centr.,' 1902, ii, 1217.

§ R. Adan, 'Internat. Cong. App. Chem.,' 1909, Sect. viiiC, 203.

content of husk and nib, of several varieties of cacao. His results are given in Table XXXVIII.

TABLE XXXVIII—*Pentosan Content of Roasted Nib and Husk.*

	Nib.	Husk (dry).
Ariba	1·29	9·97
Port au Prince	1·27	7·57
San Thomé	1·45	8·49
Caracas	1·19	7·78
Bahia	1·77	9·45
Soconusco	1·21	10·53

Luhrig and Segin* gave 7·59 per cent. to 11·23 per cent. for the pentosans found in husk against 2·51 per cent. to 4·58 per cent. found in the corresponding nibs, and many other observations of this value have been made.

König,† in estimating the amount of cellulose present in cacao husk, found that treatment with sulphuric acid and potash in the usual manner brought about an alteration in the pentosans, so that the results obtained did not represent the true amount of cellulose present.

The same author‡ recommends the estimation of pentosans by a method with phloroglucine, whilst Tollens§ and his pupils have obtained extremely accurate results by estimation of pentosans present by both volumetric and gravimetric methods, which Adan adopted for obtaining his results. These methods will be described later.

Fincke‖ has found in dry fat and ash-free husks 20·21 per cent. of crude fibre, composed of 9·88 cellulose and 9·92 lignin, against 9·28 per cent. crude fibre, composed of

* H. Luhrig and Segin, 'Zeitsch. Nahr Genussm.,' 1906, xii, 161.

† König, *ibid.*, 1898, 3.

‡ König, 'Untersuch. landwirtshaft u. gewerbe Stoffe,' 1906.

§ Tollens, etc., 'Zeitsch. angew. Chem.,' 1896, 712, 749, etc.

‖ Fincke, 'Zeitsch. Nahr Genussm.,' 1907, xiii, 265.

3·57 cellulose and 5·47 lignin for the dry fat and ash-free cocoa powder, prepared from the corresponding nibs.

Further discussion of the fibre, cellulose, pentosan, etc., content of cacao will be made when cocoa powders and their possible contamination or adulteration with cacao husk are considered in Chapter XXII.

ASH (3 per cent. to 9 per cent. of the raw, 3·5 per cent. to 10·5 per cent. of the roasted husk).

The most exhaustive analysis of the ash or mineral matter, obtained from cacao husk, has been made by Bensemann,* who gives the following table:

TABLE XXXIX.—*Analysis of Mineral Matter from Cacao Husk.*†

	Maracaibo	Caracas.	Trinidad.	Guayaquil Machala.	Porto Plata.
Ash dried at 100° C.—					
I. Insoluble in dilute hydrochloric or nitric acid:					
(*a*) Volatile above and dried at 100° C.	0·11	0·42	0·98	0·31	1·25
(*b*) Fixed at red heat	1·92	47·71	29·22	37·66	51·51
II. Soluble in dilute hydrochloric or nitric acid ·					
(*c*) Potassium oxide (K_2O)	31·52	11·81	25·87	23·12	12·17
(*d*) Sodium oxide (Na_2O)	4·19	3·30	2·73	1·21	2·78
(*e*) Calcium oxide (CaO)	10·13	44·46	5·10	3·50	4·40
(*f*) Magnesium oxide (MgO) . . .	9·55	4·70	5·21	4·84	4·09
(*g*) Ferric oxide (Fe_2O_3)	0·65	0·93	0·34	0·96	0·46
(*h*) Aluminium oxide (Al_2O_3) . . .	0·28	1·55	0·71	1·85	1·05
(*i*) Silicic oxide (SiO_2)	1·18	7·98	2·42	4·32	6·78
(*k*) Phosphoric anhydride (P_2O_5) . .	9·07	7·63	4·70	7·29	7·24
(*l*) Sulphuric anhydride (SO_3) . . .	3·04	1·48	3·40	1·74	2·01
(*m*) Chlorine (Cl)	1·01	0·22	1·02	0·26	0·44
(*n*) Carbonic anhydride (CO_2) . . .	25·45	5·40	16·29	11·83	4·25
(*o*) Water (H_2O)	2·14	2·50	2·26	1·17	1·66
(*p*) Oxygen (O) equivalent to chlorine.	0·23	0·05	0·29	0·06	0·10

* R. Bensemann, 'Report der analyt. Chem.,' 1885, v, 178.

† *Vide* also Chap. XI, Table XVI.

The most important variations occur in the amount of insoluble mineral matter fixed at red heat, and which would consist chiefly of silica or sand picked up during the processes of preparation of the beans for market.

Duclaux* was the first to find small quantities of copper in the ash of cacao, and Galippe,† confirming his results later, found that the greater part of the copper existed in the husk, and that in some samples of inferior chocolate examined, that metal was present in as large a proportion as 0·12 grm. to a kilo of cacao.

THEOBROMINE (0·4 per cent. to 2·0 per cent. of the raw or roasted husk).

It has already been pointed out that the theobromine, caffeine, and other alkaloids are extracted from cacao husk on the commercial scale. Dekker‡ was only able to extract 0·5 per cent. of theobromine from the husk, though Eminger§ obtained 0·76 per cent., and Wolfram‖ 0·42 per cent. to 1·11 per cent., the latter figures being obtained from the husk of Caracas beans.

To theobromine and its accompanying alkaloids are due the stimulating properties of cocoa and chocolate, from 1·0 per cent. to 3·0 per cent. being found in the nibs from which the preparations are made. The degree of roasting is an important factor in determining the amount of theobromine to be found in the roasted husks, nibs, and their preparations, as the alkaloid is volatile, subliming at 134° C. without melting.

Woskresensky¶ was the first to find theobromine in the seeds of *Theobroma cacao* to the extent of 1·3 per cent. to

* Duclaux, 'Bull. de la Soc. Chim.,' 1872, 33.
† Galippe, 'Journ. de la Pharm. et de Chim.,' 1883, vii, 506.
‡ J. Dekker, 'Rec. Trav. Chim.,' 1903, xxii, 143.
§ Eminger, 'Forsch. Ber. über Lebensmittel,' etc., 1896, iii, 275.
‖ Wolfram, 'Zeitsch. anal. Chem.,' xviii, 346.
¶ Woskresensky, 'Liebig's Annalen,' xli, 125.

4·6 per cent. This early investigator was followed by Glasson, Keller, Rochleder, and Strecker, all of whom obtained higher values than accredited at the present time. Kunze* has made a very complete study of the published analyses and methods of separation of theobromine by Weigmann, Mulder, Wolfram, Zipperer and many others, and has found their methods to be imperfect and their values inaccurate.

Fischer† was the first to synthesise theobromine, which he prepared by heating a lead salt of xanthine ($C_5H_2Pb_6N_4O_2$) with methyl iodide; the synthetic product possesses the same physiological and toxic actions as the alkaloid extracted from cacao, and has largely replaced the natural product in pharmacy.

Theobromine ($C_7H_8N_4O_2$), or dimethylxanthine, occurs as minute trimetric crystals, slightly soluble in hot water, alcohol and ether, possesses an extremely bitter taste, and sublimes without melting at 134° C. according to Kunze,* at 170° C. according to Blyth,‡ or 290° C. from the results of Schmidt and Pressler.§ Theobromine is slightly soluble in chloroform and warm amyl alcohol, but practically insoluble in benzol or petroleum ether.

Theobromine forms easily crystallisable salts, the simple neutral salts being decomposed by water into basic salts with loss of acid. An important salt of theobromine is that formed with silver nitrate, quite insoluble in water, and possessing a composition, according to Strecker, $C_7H_7AgNO_2$.

The alkaloid is precipitated by sodium phospho-tungstate and gold chloride, the former producing a yellow precipitate, while the latter yields long needle-shaped crystals.

Theobromine, like caffeine, is closely related to uric

* Kunze, 'Zeitsch. anal. Chem.,' 1894, 1.

† Fischer, 'Ber.,' xv, 453.

‡ Blyth, 'Foods, their Composition and Analysis,' 1909.

§ Schmidt and Pressler, 'Liebig's Annalen,' ccxvii, 287.

acid, and Fischer,* starting with methyl pseudo-uric acid, succeeded in synthesising the former alkaloid.

The murexide reaction is obtained with both theobromine and caffeine on treatment with chlorine water; the amilic acid so formed is rapidly dried down on a watch-glass and a drop of ammonia added, when a violet coloration readily distinguishes these alkaloids from other plant bases which do not belong to the xanthine group.

PROTEID MATTER (12 per cent. to 16 per cent. of the raw, 13 per cent. to 18 per cent. of the roasted husk), and NITROGEN (2 per cent. to 3 per cent. of the raw or roasted husk).

The nature of the proteid matter present in the husk of cacao has been but little investigated, though the large proportion which it contains makes the husks of high food value for cattle feeding, etc., only, since the undesirable nature of the other constituents renders it unfit for human consumption. The nitrogen is, however, probably present as globulin insoluble in water, but soluble in solutions of neutral salts.

The shells of beans fresh from the pod contain considerably larger proportions of proteid matter and nitrogen than the corresponding beans when cured. This is due to the decomposition of the albuminoids, such as globulin, by the agency of the proteolytic enzymes, which take a part in the fermentation process already described, and to the loss of theobromine, which seems to take place also during fermentation.†

Marcker gives from 12·7 per cent. to 14·1 per cent. of albumen, and 4·4 per cent. to 7·1 per cent. of digestible albumen, found in the husks of cacao.

* Fischer, 'Berlin. Chem. Ber.,' 1897, 1839.

† Prof. Harrison in Hart's 'Cacao.' 1900, 105.

Starch, Cacao Red, etc. (40 per cent. to 55 per cent. of the raw or roasted husk).

The remaining components of husk, constituting some 50 per cent. of the whole, are of little interest or importance, and no figures are obtainable which throw any light upon their actual composition.

This is due to the fact that such analyses of cacao husk as have been made have been carried out with a view to determining the food value for cattle feeding, etc. A. Smetham* finds 46·01 per cent. of digestible carbohydrates, and states that this figure includes all the non-nitrogenous bodies present in the husk with the exception of woody fibre and fat. G. Paris and other investigators into the value of cacao husk, for purposes of cattle food, have made indefinite analyses of this portion of the husk components, but they little more than show it to be composed of carbohydrates. It is, however, unnecessary for our purpose to attempt to define it more closely, as the nature of cacao red and starch likely to be found in the husk, and present in the kernel or nibs to a greater degree, are discussed in the next chapter, where more detailed figures have been collected.

* A. Smetham, 'Journ. Roy. Lancs. Agric. Soc.,' 1909.

CHAPTER XXI

SURVEY OF THE COMPONENT PARTS OF ROASTED CACAO BEANS—NIBS

NIBS (80 per cent. to 88 per cent. of the whole bean).

THE amount of nibs obtainable from a cacao depends upon the variety of bean and the care with which the husking and the nibbing process has been performed.

Information with regard to both possible variations has been already given, and the amount of return of nibs or cacao for use in the manufacture of cocoa and chocolate has been shown to range from 80 per cent. to 86 per cent. of the whole bean.

The composition of the kernel or nibs has been studied by many investigators, three of the most recent and important analyses being shown in the following table:

TABLE XL.—*Composition of Nib or Kernel (roasted).* *

	I.	II.	III.
Moisture	3·00	5·86	3·11
Fat	50·00	50·30	54·37
Starch	—	9·97	—
Ash	3·07	3·87	3·11
Cellulose	—	4·05	—
Pentosans	—	1·36	—
Fibre	2·80	—	—
Nitrogen	2·50	—	—
Cold water extract	11·60	—	9·67

I. N. P. Booth, 'The Analyst,' 1909, xxxiv, 144.
II. R. Adan, 'Internat. Cong. App. Chem.,' viiiC, 203.
III. F. Bordas, 'Internat. Cong. App. Chem.,' viiiC, 188.

* *Vide* also Chap. X, Tables XI and XII.

The analyses shown are divided by the same three authors into results obtained from different varieties of beans, thus :

TABLE XLI.—*Composition of Nibs or Kernels (roasted) from different Varieties of Cacao.*

	Caracas.			Trinidad.		African.		Grenada.		Guayaquil.		Bahia.	
	I.	II.	III.	I.	III.	I.	II.	I.	III.	I.	II.	I.	II.
Moisture .	—	7·48	3·27	—	2·90	—	5·71	—	2·86	—	8·52	—	3·71
Fat . .	—	49·24	52·56	55·70	54·50	50·20	50·20	50·80	55·26	—	50·07	44·4	50·19
Starch . .	—	9·85	—	—	—	—	13·27	—	—	—	9·10	—	9·61
Ash . .	3·24	3·92	3·81	2·73	3·30	2·52	3·89	2·60	2·90	3·16	3·89	2·68	3·24
Cellulose .	—	4·24	—	—	—	—	4·33	—	—	—	3·70	—	3 93
Pentosans .	—	1·19	—	—	—	—	1·45	—	—	—	1·29	—	1·77
Fibre . .	—	—	—	2·48	—	—	—	2·94	—	—	—	—	—
Nitrogen .	—	—	—	2·32	—	1·84	—	2·26	—	—	—	1·98	—
Cold water extract .	—	—	10 87	12·00	9·87	11·80	—	9·80	9·15	11·40	—	9·50	—

More detailed analyses have been made from time to time, and the three following are typical of the general results obtained :

TABLE XLII.—*Analyses of Roasted Cacao Nibs.*

	I.	II.	III.
Moisture	5·23	6·3–8·5	3·7–4·4
Fat	50·44	46·9–52·1	45·3–54·4
Albuminoids	13·26	11·6–21·1	7·4–13 0
Gum	2·17	—	—
Cellulose	6·40	3·3–6·6	—
Alkaloids	0·84	0·3–0·5	—
Cacao red	2·20	—	—
Ash	2·75	2·9–4·8	2·4–3·9
Astringent matters	6·71	} 7·2–8·6	} 26·3–39·4
Cane sugar	—		
Starch	4·20	8·7–12·6	

I. J. Bell, 'The Chemistry of Foods,' 1887, 76.
II Zipperer, 'Untersuch. über Kacao, etc.,' 56, 57.
III. Heisch, 'The Analyst,' I, 142.

The following table, to be found in the records of the Society of Arts, 1874, contains the most important analyses made up to that time.

TABLE XLIII.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Fat . . .	53·10	52·00	51·00	50·00	56·00	15·00–49·00	42·67	50·00
Albuminoid substances . .	18·70		—	—	17·00	13·00–18·00	—	—
Albumen . .	—	20·00	—	20·00	—	—	—	18·00
Fibrin . . .	—		—	—	—	—	—	
Gluten . . .	—	—	20·00	—	—	—	12·21	—
Sugar . . .	—	—	—	—	—	0·60	—	—
Starch . . .	10·91	10·00	22·00	7·00		14·00–18·00	19·03	10·00
Gum . . .	7·75	—		6·00		—	6·40	8·00
Lignin . . .	0·90	—	—	—	22·00	—	—	—
Cellulose . .	—	2·00	—	—		6·08	5·95	—
Woody fibre . .	—	—	—	4·00		—	—	—
Colouring matter .	2·01	Traces	—	2·00	—	3·05–5·00	3·96	2·60
Water . . .	5·20	10·00	5·00	5·00	—	5·06–6·30	5·98	6·00
Theobromine .	—	2·00	2·00	2·00	1·50	1·02–1·50	0·90	1·50
Salts . . .	—	4·00	—	4·00	—	—	—	—
Ash . . .	—	—	—	—	—	3·05	2·90	3·60
Parts unaccounted for . . .	1·43	—	—	—	3·50	9·14	—	0·30
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

A large number of analyses of the different varieties of beans may be found on referring to the papers mentioned in the footnote, but those given in Table XLI may be taken as typical of analyses of commercial value to show the slightly varying composition of several important cacaos.

MOISTURE (6 per cent. to 8 per cent. of the raw, 4 per cent. to 7·5 per cent. of the roasted kernel.)

The variations in water content of the kernel are due to the same three causes prevailing to alter the percentage of moisture in the husk already given, namely, degree of drying before shipment, treatment during transit and storage, and temperature and degree of roasting. A large percentage of moisture is obviously undesirable in the

kernels, as it both tends to deteriorate the flavour of the bean by encouraging fungoidal growth, and to destroy the keeping property of the cocoa or chocolate prepared from the damp nibs.

Fat (45 per cent. to 53 per cent. of the raw or roasted kernel).

The percentage of fat in the kernel is a variable quantity, depending upon the variety of bean and degree of roasting.

Harrison has pointed out that if, during fermentation, germination of the seed is allowed to take place, the fat is one of the first constituents of the kernel to be attacked after the sugars have been absorbed. This factor may, therefore, play an important part in determining the amount of fat present in any variety, as in certain districts germination is allowed to take place before fermentation to a greater or less degree, depending upon the customary procedure of fermentation in any district.

Davies and McLellan,* however, state that the percentage of fat found is independent of the locality in which the bean originated.

The following collected figures, obtained from one variety of beans, show some exceedingly contradictory results, and tend to prove that the processes of fermentation and roasting are somewhat overrated as to their importance on final yield of fat, when compared with individual results of other observers.

	Unfermented.	Mildly fermented.	Fully fermented.	Highly fermented.	Very high roast.	Very low roast.
Fat per cent.	54·68	56·73	57·35	58·23	54·0	52·7

It is our experience that in the case of a very high roast (above 150° C.), or a prolonged roasting at a normal temperature, the percentage of fat will be lowered, while

* *Vide* Chapter X.

the effect of roasting at a reasonable temperature will always raise the fat content of the nibs, results opposed to the figures given above.*

The distribution of fat in various parts of the cacao pod and bean has been the subject of several researches; Harrison† has estimated the proportion of the different constituents of cacao in the kernels, cuticles and pulp, and external pod of the fresh cacao fruit, and gives the values for fat respectively as 30·60 per cent., 0·42 per cent., and 0·14 per cent., the proportion of moisture being respectively 36·57 per cent., 83·03 per cent., and 84·54 per cent.

Bordas has found the percentage of fat in different parts of roasted cacao to vary as follows:

	Per cent.
Cacao nibs (eleven varieties) .	50·20 to 56·14
Cacao dust (from nibbing machine)	20
Germ	3·5
Husk	2·0 to 11·0

The general characteristics of cacao butter have been extensively discussed in the foregoing chapter, where also will be found all the important chemical and physical constants for the fat.

Starch (4 per cent. to 12 per cent. of the raw or roasted kernel) and other Carbohydrates (8 per cent. to 13 per cent. of the raw or roasted kernel).

The starch present in cacao is similar in composition to that found in other vegetable seeds. It is readily gelatinised by boiling water, is turned blue by iodine, and converted, by the action of dilute mineral acids and diastase, into glucose.

The granules of cacao starch are very minute, and the concentric rings, showing their composite structure, can only be detected with a high-power microscope.

* *Vide* Chapter X.

† Harrison in Hart's 'Cacao,' 1900, 90.

Bordas has made careful determinations of the quantity of starch to be found in different cacaos, and states that the amount is practically constant for all commercial varieties. His results are as follows:

TABLE XLIV.—*Starch in different varieties of Cacao.*

	Starch in 100 parts of cacao.	Starch calculated for 100 parts of cacao insoluble in water.
Sancheize	9·60	28·90
Bahia	9·00	27·69
Haiti	8·50	26·10
St. Lucia	9 29	28·49
Trinidad	9·60	29 77
Grenada	9·35	28·56
Maragnan	8·88	27·66
Carupano	9·93	30·30
Porto Plata	10·00	30·50
Caracas	9·93	29·81
Guadeloupe	8·66	26·00
Mean	9·34	28·50

Maurenbrecker and Tollens* have made a close study of the carbohydrates occurring in cacao, and have succeeded in detecting l. arabinose, d. galactose and glucose (from hydrolysis of the starch), but no xylose was found.

The same authors estimated the amount of pentosans, already discussed in the preceding chapter, and found them to be present to the extent of 2·25 per cent. in the nibs or kernels, and 9·02 per cent. to 9·09 per cent. in the husks; these figures are in close agreement with those obtained by Dekker,† who found 2·17 per cent. to 2·41 per cent. of pentosans in the kernel, and 8·18 per cent. to 9·63 per cent. in the husks.

Adan‡ obtained figures equivalent to 1·53 per cent. of pentosans for the nibs, and 9·96 per cent. for the dry husks.

* A. D. Maurenbrecker and B. Tollens, 'Ber.,' 1906, xxxix, 3576.

† Dekker, 'Chem. Centr.,' 1902, ii, 1218.

‡ R. Adan, 'Bull. Soc. Chim. Belg.,' 1907, xxi, 211, and 'Internat. Cong. App. Chem.,' 1909, viiiC, 203.

FIBRE (2 per cent. to 5 per cent. of the raw or roasted kernel).

The amount of fibre found in the nibs is entirely dependent upon the care with which the husk or fibrous matter is separated from the inner kernel. It has been pointed out by Tollens, König and others, that the estimation of cellulose is not a true guide to the quantity of fibre present, as the existence of pentosans hinders the correct determination.

The fibrous wall of the cacao bean is composed of pentosans embedded in many other matters, such as cacao red, mineral matter, etc., and it is in the estimation of the pentosans that addition of husk to cacao preparations is best detected. If properly freed from husk, the nibs should not contain more than 4·5 per cent. of crude fibre, though Filsinger* obtained values ranging from 2·8 per cent. to 5·4 per cent. for different varieties of beans by estimating the crude fibre by a method described by König. Such a figure for crude fibre would approximately equal 2·5 per cent. of pentosans, constituting a little more than 50 per cent. of the total crude fibre found.

Welmans† obtained an average of 13·3 per cent. of husk from raw, and 12·4 per cent. from roasted nibs. His figures are obviously too high for a well-husked kernel, and it is to be assumed that they comprise the ash, fat, and other components of the husk, besides crude fibre.

Bordas, in his communication to the International Congress of Applied Chemistry, 1909, has estimated the amount of cellulose present in various cacaos. He points out the value of cellulose estimation on the ground that any addition of matter containing woody fibre, such as

* Filsinger, 'Zeitsch. öffent. Chemie,' 1900, 223.

† P. Welmans, 'Zeitsch. öffent. Chemie,' 1901. vii. 491.

husks, cacao waste, germs, etc., will increase the proportion of cellulose and diminish the starch content of the kernels or of the cacao mass prepared from them.

His results will be found in Chap. XI, Table XV.

Ash (3 per cent. to 4 per cent. of the raw or roasted kernel).

The percentage of ash in cacao beans has been shown by the investigations of a number of observers to vary considerably. This is usually the case in the mineral matter obtained from food stuffs of vegetable origin.

Bensemann* has made careful analyses of the ash obtained from various varieties of cacao, and his figures obtained from the mineral matter of Caracas and Trinidad

Table XLV.—*Analyses of Mineral Matter from Cacao Nibs.*

	Caracas.		Trinidad.	
	I.	II.	I.	II.
Potassium oxide (K_2O)	33·84	32·50	30·85	32·28
Sodium oxide (Na_2O)	0·77	2·50	1·96	1·90
Calcium oxide (CaO)	5·03	4·30	4·64	3·54
Magnesium oxide (MgO)	15·15	13·00	16·06	15·43
Ferric oxide (Fe_2O_3)	0·22	1·82	0·49	0·74
Aluminium oxide (Al_2O_3)	0·33		0·49	
Silicic oxide (SiO_2)	0·21	7·00	0·17	7·00
Phosphoric anhydride (P_2O_5)	29·30	25·60	28·62	28·38
Sulphuric anhydride (SO_3)	2·74	3·10	3·96	3·80
Chlorine (Cl.)	0·34	0·20	0·43	0·40
Carbonic anhydride (CO_2)	8·44	7·98	8·95	5·53
Water(H_2O)	1·98	—	2·78	—

I. R. Bensemann, 'Repert analyt. Chem.,' 1885, v, 178.
II. Dr. Bordas, 'Internat. Cong. App. Chem.,' viiiC, 188.

cacaos are here shown compared against those obtained by Bordas.

Bordas' figures for silicic oxide include sand, and those for carbonic anhydride are estimated by difference.

* R. Bensemann, 'Repert analyt. Chem.,' 1885, v, 178.

It will be seen that the most important component of cacao ash is potassium oxide (K_2O), which amounts to about one third of the total mineral matter.

The potassium is probably present in the original bean as salts of the plant acids, and as carbonate.

The lime, or calcium oxide, is present as oxalate to the extent of 0·2 per cent. of the nib, other alkaline oxalates being found by Girard* to amount to 0·15 per cent. of the roasted kernel or nib of Trinidad cacao.

The amount of potassium salts present is of interest when the contentions, that the addition of alkali, such as potassium hydrate or carbonate, to cocoa or chocolate is injurious to health, are considered.

Luhrig and his workers† have estimated the alkalinity of the aqueous extract of cacao beans, and from the average of twenty-eight samples obtained a value of 0·99 per cent. of alkali as K_2CO_3 on the fat-free cacao. One sample of cacao powder yielded as much as 2·11 per cent. of alkali soluble in water, calculated as K_2CO_3 on dry cocoa powder, after 30 per cent. of fat had been extracted. The same author points out that if the amount of alkali calculated as potassium carbonate (K_2CO_3) exceeds 3 per cent. the addition of alkali is certain.

These figures are considerably in excess of those obtained by Booth‡ already given.

Proteid Matter (10 per cent. to 17 per cent. of the raw or roasted kernel) and Nitrogen (1·5 per cent. to 2·5 per cent. of the raw or roasted kernel).

Leffman and Beam§ have given some results obtained by Stutzer on the nitrogenous constituents of cacao.

* C. Girard, 'Internat. Cong. App. Chem.,' 1909, viiiC, 179.

† Luhrig, etc., 'Zeitsch. Nahr. Genussm.,' 1905, ix, 257.

‡ N. P. Booth, 'The Analyst,' 1909, xxxiv, 143.

§ Leffman and Beam, 'Food Analysis,' 1901, 275–282.

Stutzer* found that the nitrogenous components were of three types:

(1) Non-proteids not precipitated by $Cu(OH)_2$, such as theobromine, caffeine, and amido compounds.

(2) Digestible albumen insoluble in water in the presence of $Cu(OH)_2$, but soluble when treated with acid, gastric juice and alkaline pancreatic extract.

(3) Insoluble and indigestible nitrogenous matter.

The analyses of the nitrogenous constituents are given as follows:

	I. Per cent.	II. Per cent.	III. Per cent.
Nitrogen as soluble compounds (alkaloidal) . . .	31·43 .	26·95 .	29·79
Nitrogen as digestible albumen	33·34 .	40·61 .	22·62
Nitrogen as indigestible matter	33·33 .	32·44 .	47·83

The three nitrogen-bearing constituents were present, according to the author, in approximately equal proportions. The results obtained by other observers do not agree with Stutzer's figures: thus Bell gives albuminoids (proteid matter, or digestible and indigestible proteid) as 13·26 per cent., and alkaloids as 0·84 per cent. of the kernel. Zipperer finds 11·6 per cent. to 21·1 per cent. of albuminoids, and 0·3 per cent. to 0·5 per cent. of alkaloids in the kernel.

The percentage and quality of the total nitrogen-containing components of cacao are of little commercial importance, however, and Stutzer's figures are obviously open to criticism, owing to the large error which occurs on multiplying the small quantity of nitrogen, actually found for each type, to read as percentage of total nitrogen.

The amount of nitrogen multiplied by 6·25 gives approximately the total albuminoid matter found in cacao.

* Stutzer, 'Zeitsch. phys. Chemie,' ii, 207.

THEOBROMINE (0·9 per cent. to 3 per cent. of the raw or roasted kernel) AND CAFFEINE (0·05 per cent. to 0·36 per cent. of the raw or roasted kernel).

The general chemical and physical characteristics of the alkaloids, present in cacao, have been given in the previous chapter.

The amount of these alkaloids found in the nibs varies very considerably, both with the variety of the bean and the care of the observer. Great differences are to be found in the alkaloid estimation of early and recent investigators; thus Zipperer finds 0·3 per cent. to 0·5 per cent. of total alkaloids in the roasted nibs of cacao, and Eminger 1·0 per cent. to 2·3 per cent. of theobromine and 0·05 per cent. to 0·36 per cent. of caffeine.

TABLE XLVI.—*Theobromine in different varieties of Cacao.*

	I.	II.	III.	IV.	V.
Caracas	1·43	1·63	0·50	1·13	1·38
Guayaquil	0·9–1·2	1·63	0·30	0·86	—
Domingo	1·98	1·66	—	—	—
Bahia	2·04	1·64	—	1·08	—
Puerto Cabello	1·02	1·46	0·52	—	—
Maracaibo	1·84	—	—	1·03	—
Ceylon	2·06	—	—	—	—
Java	2·34	—	—	1·16	—
Trinidad	1·98	—	0·42	0·85	1·44
Para	1·08	—	—	—	1·28
Grenada	1·90	—	—	0·75	1·60
Surinam	1·83	—	0·54	0·93	—
Cameroon	1·83	—	—	—	—
San Thomé	2·09	—	—	—	—
Haiti	2·07	—	—	—	—

I. A. Eminger, 'Apoth. Zeit.,' 1896, 716.
II. Wolfram, 'Zeitsch. anal. Chemie,' xviii, 346.
III. Zipperer, 'Untersuch. über Kakao, etc.,' 1886, 56.
IV. Ridenour, 'Amer. Journ. Pharm.,' 1895, lxvii, 202.
V. L. Maupy, 'Journ. Pharm. Chimie,' 1897 [6], v, 329.

Kreutz* points out a possible explanation of these discrepancies, and states that theobromine exists in the bean

* A. Kreutz, 'Zeitsch. Nahr. Genussm.,' 1908, xvi, 579.

partly as the free alkaloid and partly in the form of a glucoside, which can only be separated after treatment with an acid. The same author finds from 1·5 per cent. to 2·4 per cent. of free, and from 1·6 per cent. to 2·8 per cent. of combined alkaloids in the kernels of cacao.

Table XLVI shows the results obtained by several other observers

CACAO-RED (2 per cent. to 5 per cent. of the raw or roasted kernel).

The colouring matter of cacao is produced during the oxidation of, or the free admission of air to, the beans.

When fresh, the Criollo variety of bean is white or nearly so, the Calabacillo variety being often of a deep purplish tint, while the Forastero cacao, occupying the intermediate position, shows only a faintly coloured kernel.

Harrison has shown that there is a loss of cacao-red in all three varieties during fermentation, a total loss of 0·27 per cent. occurring in a mixture of Calabacillo and Forastero beans.

The formation of cacao-red is of peculiar importance to the manufacturer, who looks to this agency for the pronounced chocolate colour of his goods.

The variety of bean selected and careful roasting are the most important factors in obtaining a satisfactory colour for cocoa or chocolate. Schweitzer* has made some investigations into the formation of cacao-red in the bean, and compares it with the production of colouring matter in the oak, kola nut and quinine, tracing it to the decomposition of a glucoside, "cacaonin," during fermentation, when theobromine, caffeine and glucose are also produced.

* C. Schweitzer, 'Pharm. Zeit.,' 1898, 389.

Hilger* also has closely followed the production of cacao-red during the fermentation of the bean, and concludes that the colouring matter isolated in the ordinary way is a mixture of non-nitrogenous cacao-red and some glucoside.

True cacao-red can be isolated by treating the roasted beans first with petroleum ether to remove the fat and part of the free theobromine, then with water to extract the remainder of the theobromine, caffeine, sugars and salts, and finally with alcohol to extract the cacao-red.

A substance having a formula $C_{17}H_{12}(OH)_{10}$ is obtained in this way, closely akin to tannin, which it resembles in yielding formic acid, acetic acid and pyrocatechin on treatment with potassium or sodium hydrate.

Blyth† states the fat-free cacao is only partially deprived of its cacao-red by solvents unless a mineral acid has been previously added. After the addition of a few cubic centimetres of hydrochloric acid the red colouring matter is dissolved with ease by amyl or ethyl alcohol.

Cacao-red so produced is insoluble in ether or petroleum ether, but slightly soluble in carbon bisulphide. It is a sensitive reagent to acid and alkali, mineral acids causing a red coloration with violet shimmer, alkalis usually striking a dirty green. The aqueous solution of cacao-red of this form is bitter and astringent, and forms precipitates with salts of iron, copper and silver.

Organic Acids.

Tartaric acid (free), about 0·15 per cent.	of the raw kernel.
Acetic acid (free), about 0·25 per cent.	
Oxalic acid (total), about 0·35 per cent.	

Harrison, who has made a complete study of the

* Hilger, 'Apoth. Zeit.,' 1892, 469; also 'Deutsch. Viertel. öffent. Gesund.,' 1893, 3.

† A. W. Blyth, 'Foods, their Composition and Analysis,' 1909, 363–375.

changes occurring in cacao during fermentation, has found that tartaric acid is present in larger proportions in the fermented and cured beans than in those simply dried.

The same remarks apply to the quantity of free acetic acid found, though in this case the dried beans were found to contain none, or only negligible quantities, whereas the fermented and cured beans contained as much as 0·7 per cent.

The amount of free tartaric acid contained by the fresh beans (0·25 per cent.) diminished to 0·2 per cent. during the process of fermentation, and to 0·12 per cent. during simple drying.

The free acetic acid, which was "*nil*" in the fresh beans, increased to 0·33 per cent. during fermentation and curing, and was "*nil*" after the fresh beans had been simply dried.

The quantities of these two acids in the free state were found by the same author to vary slightly with the three varieties of cacao, Criollo, Forastero, and Calabacillo. The differences are, however, small, and of no commercial importance.

The acetic acid can be detected in beans that have been fermented by the vinegary smell, which, during the process of roasting, it is so desirable to remove.

The presence of oxalic acid in the vegetable kingdom has been recognised since the commencement of the nineteenth century.

Fourcroy and Vauquelin* stated that this acid was to be found in almost every plant. The method by which their approximate results were obtained was by means of the microscope. It was as recently as 1900 that the first reliable method for the estimation of oxalic acid in cacao was published, the outcome of continuous research on the

* Fourcroy and Vauquelin, 'Journ. Phys.,' lxviii, 429.

parts of Neubauer,* Schultzen,† Salkowski,‡ Albahary§ and others. The method was based on the fact that 100 grs. of ether dissolve 1·27 grs. of oxalic acid, and that the solubility of the acid could be increased by the addition of alcohol.

Gautier gives figures found by Esbach for the oxalic acid content of several vegetable food-stuffs, thus:

	per cent.
Cocoa powder	0·45
Chocolate	0·09
Black tea	0·38
Infusion of tea	0·21
Coffee	0·01
Rhubarb	0·25

Girard has recently made some very careful estimations of the amount of oxalic acid present in cacao beans. The following table shows his results obtained from Trinidad cacao:

Table XLVII.—*Oxalic Acid present in Trinidad Cacao.*

	Roasted beans.	Raw beans.	Roasted nibs.	Raw nibs.	Roasted husk.	Raw husk.	Roasted germ.
Calcium oxalate . . .	0·195	0·191	0·221	0·216	0·121	0·119	0·240
Oxalic acid due to calcium oxalate	0·137	0·163	0·155	0·152	0·198	0·084	0·169
Oxalic acid due to alkaline oxalate	0·172	0·134	0·160	0·158	0·085	0·189	0·150
Total oxalic acid . . .	0·309	0·297	0·315	0·310	0·283	0·273	0·319
Water	3·76	5·44	3·56	4·64	9·04	11·52	3·50
Total oxalic acid per 100 parts of dry cacao . .	0·321	0·314	0·326	0·325	0·301	0·301	0·321

From an examination of the oxalates found, the same author concludes that:

* Neubauer, 'Zeitsch. anal. Chem.,' 1868, ii, 499, and vii, 225.

† Schultzen, 'Reichert und Dubois Reymond's Arch.,' 1868, 718.

‡ E. Salkowski, 'Zeitsch. phys. Chem.,' x, 120.

§ J. M. Albahary, 'Compt. Rend.,' cxxxvi, 1681, etc.

(1) Trinidad cacao contains oxalic acid in the same degree as sorrel, spinach, and rhubarb.

(2) Oxalic acid is to be found in approximately the same proportion in the beans, nibs, husk, and germ.

(3) Roasting has little or no effect on the oxalic acid content of the products.

(4) A considerable proportion of the oxalic acid exists in the state of alkaline oxalates.

CHAPTER XXII

COCOA POWDERS AND CHOCOLATES, AND THEIR COMPONENT PARTS

The component parts of cocoa powders should be the same as those of the nibs, already dealt with in the last chapter. During the preparation of cocoa powder, however, a certain quantity of fat is extracted, usually about 30 per cent. of the total fat present, and consequently the other components are found in the powders in correspondingly larger proportions.

Again, the cocoas may have been treated with alkalis, which, if carbonate or hydrate of the fixed alkalis, will cause an increase in the amount and the alkalinity of the ash found.

Chocolate powders, on the other hand, usually consist of cocoa powder or cacao mass mixed with sugar, and frequently also with starch of potato, sago, arrowroot, etc.

Plain chocolates, as distinguished from those fancy goods, which consist of fruit jelly, nougat, almonds, sugar fondant, and other centres covered with a thin coating of chocolate, should consist of cacao mass, sugar, and possibly added cacao butter only.

Milk chocolates should contain the solids of fresh full-cream milk, besides those ingredients which go to make up plain eating chocolates.

Nut chocolates, coffee chocolates, etc., should consist of plain chocolate with the addition of the ingredients which give the name to the speciality.

COCOA POWDERS.

In Chapter XIII, Tables XX, XXI, and XXII, will be found analyses of many varieties of commercial cocoa powders. It is unnecessary, therefore, to reproduce them here, though it is desirable that some average analyses should be given for easy reference.

In the following table will be found figures for four typical varieties of cocoas: (1) ordinary cocoa powder from expressed cacao nibs; (2) cocoa powder treated with fixed alkali; (3) cocoa powder treated with ammonia; (4) adulterated cocoa powder (given by Booth).

Where it has been found possible, one author's results have been supplemented with those obtained by another observer, who gives closely agreeing figures for the main components.

TABLE XLVIII.—*Analyses of Cocoa Powders.*

	I.	II.	III.	IV.
Moisture	4·33	4·53	6·56	2·40
Total ash	4·28	8·19	5·18	2·75
Alkalinity as K_2O	1·00	3·68	—	—
Fat	30·95	29·78	27·34	0·86
Extractive soluble in water	18·50	17·45	—	—
Theobromine	1·36	0·69	1·98	—
Starch	16·07	21·26	—	—
Albumen	12·78	17·03	10·50	—
Fibre	3·89	4·38	4·00	10·90
Foreign starch	*Nil*	*Nil*	*Nil*	30·00
Character of starch	—	—	—	Sago
Sugar	*Nil*	*Nil*	*Nil*	38·00

MOISTURE (2·25 per cent. to 5·0 per cent. of cocoa powder).

A good cocoa powder should never contain more than 5 per cent. of moisture, as an amount exceeding this limit tends to "ball" the powder and to render it liable to the attack of mildew, which would seriously injure the flavour.

ASH (3 per cent. to 5 per cent. of cocoa powder, 5 per cent. to 11 per cent. of "soluble" cocoa powder).

In Chapter XIII, Table XXIII, will be found analyses of the ash obtained by incinerating some cocoa powders of commerce, and performed by Girard.

Bensemann and Bordas have also made careful analyses of the ash obtained from different varieties of cacao beans.

The following table shows the collected results of the different authors:

TABLE XLIX.—*Analyses of Ash of Cacao Mass and Cocoa Powders.**

	I.	II.	III.
Potassium oxide (K_2O)	32·25	29·53	22·97
Sodium oxide (Na_2O)	2·17	2·44	22·32
Calcium oxide (CaO)	3·96	3·39	1·25
Magnesium oxide (MgO)	16·14	16·57	10·33
Ferric oxide (Fe_2O_3)	0·36	0·49	0·83
Aluminium oxide (Al_2O_3)	0·33	0·08	0·15
Silica (SiO_2)	0·19	1·67	0·77
Phosphoric anhydride (P_2O_5)	31·59	32·41	24·13
Sulphuric anhydride (SO_3)	3·07	2·58	1·84
Chlorine (Cl)	0·29	0·61	0·96
Carbonic anhydride (CO_2)	6·80	10·35	14·67
Water (H_2O)	1·94	*nil*	*nil*

I. Ash from cacao mass by R. Bensemann, 'Repert analyt. Chem.,' 1885, v, 178.

II. Ash from Menier cocoa powder by C. Girard, 'Internat. Cong. App. Chem.,' 1909, viiiC, 186.

III. Ash from Van Houten's cocoa powder by C. Girard, *ibid.*

From these figures it will be seen that the most important differences arise in the values of sodium oxide and carbonic anhydride in samples I and III. In the latter case it is certain that sodium hydrate or carbonate was used for rendering the cacao "soluble," the ash in either case being capable of estimation as sodium oxide and

* *Vide* also Chapter XI, Table XVI.

carbonic anhydride, due to the absorption of the latter from the air by the alkaline hydrate.

Bordas* elsewhere has pointed out that the quantity of added alkali present in imported cocoas should be regulated, Belgium, Italy and Switzerland already prohibiting the sale of cocoa powders containing more than 3 per cent. of added alkaline carbonate.

The same author points out that natural cacao mass contains from 2·46 per cent. to 3·05 per cent. of alkali, calculated as potassium oxide on the fat-free substance, whilst samples of "soluble" cocoa examined have shown from 4·82 per cent. to 6·41 per cent. of added alkali calculated on the same basis.

Stutzer† has estimated the soluble constituents of many samples of cocoa, and states that there is nothing to be gained by the addition of alkaline carbonates. With this opinion we do not agree.‡

Matthes,§ in conjunction with Rohdlich, has formed the opinion that the estimation of silica (SiO_2), previously suggested by the former author, is no indication of the amount of husk added to a cocoa powder, as they found, in twenty samples of cocoa examined, figures ranging from 0·02 per cent. to 0·88 per cent. of silica. Except in extreme cases of adulteration with husk this is true, Bensemann finding from 1·2 per cent. to 8·0 per cent. of silica in the husk and 0·2 per cent. in the nibs, whilst Bordas has given from 0·5 per cent. to 7·3 per cent. of silica and sand in the nibs, and 19·10 per cent. in the husk.

Fat (22 per cent. to 35 per cent. of cocoa powder).

According to the degree of compression to which the cacao nibs have been subjected, the percentage of cacao fat

* F. Bordas, 'Ann. Falsif.,' 1910, iii, 61.

† A. Stutzer, 'Zeitsch. angew. Chem.,' 1892, 510.

‡ *Vide* Chapters XII and XIX.

§ Matthes and Rohdlich, 'Zeitsch. öffent. Chem.,' 1908, xiv, 166.

or butter found in a cocoa powder will vary. The methods of expression of cacao butter have already been described in Chapter XII.

Clayton* has published analyses of a variety of cocoa powders, which show percentages of fat ranging from 22·30 per cent. to 33·11 per cent.

There have been many other analyses of cocoa powders made by different observers, but in all cases, except in those where adulteration has been carried to an extreme, the fat content of cocoa powders varies between 22 per cent. and 35 per cent.†

The fat extracted should give the chemical and physical constants already detailed in Chapter XX, if pure cacao has been used and no addition of foreign fat has been made.

Beythien,‡ who has also examined a large number of commercial cocoa powders, has stated that out of 58 samples of powders of German manufacture, 28 contained less than 20 per cent. of fat, and 30 samples less than 25 per cent.; of the 65 samples of Dutch cocoas examined 49 contained less than 20 per cent., 3 less than 25 per cent. and 13 samples over 25 per cent. of fat; all the Swiss samples contained over 25 per cent. of fat.

Extractive Soluble in Water (17·5 per cent. to 18·5 per cent. of cocoa powder).

The cold water extract of the nib or kernel of cacao ranges from 9·5 per cent. to 12·5 per cent., whilst the figure for fat-free cacao amounts to approximately 24 per cent. Florence Yaple,§ however, gives considerably lower figures, which we are unable to reconcile with those of more recent observers.

The soluble extractive, which will include sugars, gums,

* E. J. Clayton, 'Chem. News.' 1902, lxxxvi [2227], 51.

† *Vide* also Chapter XIII, Table XXI.

‡ Beythien, 'Zeitsch Nahr. Genussm.,' 1908, xvi, 579.

§ Florence Yaple, 'Chem. Zeit.,' 1895, Rep. 21, 240.

soluble starch, and soluble mineral matter, etc., is a useful indication to the possible adulteration of a powder with sugar and alkali, the addition of either tending to increase the figure for soluble extractive.

The alkalinity of the matter soluble in water will be a guide to the extent of addition of alkali.

The estimation of soluble extractive is of greater importance in the analysis of chocolate or chocolate powders.

Theobromine (0·70 per cent. to 2·70 per cent. of cocoa powder).

The quantity of theobromine found in a cocoa powder will depend largely upon the degree of roasting to which the beans have been subjected (*vide* Chapter X). E. J. Clayton* found from 0·83 per cent. to 2·69 per cent. of theobromine and from 0·02 per cent. to 0·66 per cent. of caffeine in commercial cocoa powders. Girard gives from 1·04 per cent. to 2·24 per cent. of theobromine.

The estimation of theobromine in cocoa powders is of some importance, as the exhilarating and stimulating properties of cocoa are largely due to this alkaloid.

Starch (2·0 per cent. to 11·0 per cent. of cocoa powder).

The quantity of natural starch found in cacao is very variable. Its estimation, therefore, is of little value either as a check upon the amount of cacao present or upon the addition of foreign starches, unless the latter are present in large proportions, and have been previously detected under the microscope.

Many observations of starch content of cocoa powders have been made, but they are of little or no importance to the technical chemist or manufacturer.

The addition of foreign starches can readily be detected under the microscope, when the form of the granules of

* E. J. Clayton, 'Chem. News,' 1902, lxxxvi [2227], 51.

starches, likely to be used commercially as adulterants, can be recognised.

FIBRE (2·5 per cent. to 6·5 per cent. of cocoa powder).

It has previously been pointed out that the estimation of fibre is an indication to the extent of adulteration with, or inclusion of, cacao husk.

The inclusion of cacao husk, whether intentional or through carelessness, is a matter of great importance, as many convictions have followed the sale of "cocoa powder" consisting in part or in the main of cacao husk. Some such cases have already been referred to in Chapter XVII.

Probably the most complete investigation into the detection of added husk has been made by Adan,* who not only has estimated the cellulose and pentosan content of different varieties of cacao beans, but has carried out analyses of the cocoa powders prepared from them. The direct connection between the estimation of pentosans and the amount of husk present in any cacao has been given in Chapter XX, and in Table XXXVII will be found Adan's results for the nibs and husk of various cacaos.

TABLE L.—*Cellulose and Pentosan Content of Cacao Powders of known Origin.* †

	Moisture.	Fat.	Ash.	Cellulose.	Pentosans.	
					Initial substance.	Powder with 30 °/₀ of fat.
Ariba	1·30	53·78	3·21	2·67	1·73	3·26
Port au Prince	0·83	55·69	3·56	3·14	1·58	3·73
San Thomé	0·79	51·23	3·34	3·01	1·55	3·46
Caracas	0·71	51·72	3·47	2·89	1·54	3·28
Bahia	0·69	54·77	3·29	3·09	1·71	3·43
Soconusco	1·01	55·98	3·13	2·91	1·57	3·23
Average	0·88	53·86	3·33	2·95	1·61	3·40

* R. Adan, 'Internat. Cong. App. Chem.,' 1909, viiiC, 204.

† These cocoa powders were, however, obviously obtained by merely grinding the roasted nibs, and were not even partially defatted.

Table L shows the same author's results obtained on the cocoa powders prepared from the different cacaos.

Hehner and Sketchley* have estimated the pentosan and crude fibre content of several cocoa powders and cocoa shell powders. The following results obtained by these two authors are of interest.

TABLE LI.—*Pentosan and Crude Fibre in Cocoa Powders and Cocoa Shell Powders.*

	Pentosan.	Crude fibre.
Van Houten's cocoa	2·00	6·00
Cadbury's cocoa	1·82	7·15
Cocoa shell powder I	8·98	—
Cocoa shell powder II	8·03	11·95

ALBUMEN (10 per cent. to 17 per cent. of cocoa powder).

The total nitrogen found in cocoa powders amounts as a rule to 3 per cent., or to an equivalent of, approximately, 19 per cent. of proteid matter, if all the nitrogen present is attributed to this component.

In reality Dekker† has shown that about 90 per cent. of the total nitrogen is due to proteid matter, the remaining 10 per cent. resulting from theobromine.

ORGANIC ACID, OXALIC ACID (0·4 per cent. to 0·65 per cent. of cocoa powder).

Girard, in his paper frequently referred to, delivered at the Seventh International Congress of Applied Chemistry, has shown that the oxalic acid is largely present in cacao as alkaline oxalates, and his figures, which are the most reliable up to date, tend to show that the oxalic acid is not destroyed during roasting or removed during expression of fat.

* Hehner and Sketchley, 'The Analyst,' 1899, xxiv, 178.
† S. Dekker, 'Chem. Centr.,' 1902, ii, 1217.

Sucrose, Cacao-red, etc.

The remaining components of cocoa powders are of little importance to the technical chemist. Sucrose is found only in minute quantities, and only traces of reducing matters have been notified by the most reliable observers. This is of interest when chocolate and chocolate powders are examined, to which cane-sugar has been added during preparation.

The colour of cocoa depends upon the cacao-red present, but the quantities found are strictly comparable with the results given in Chapter XXI for the nibs, after allowance has been made for the removal of some 30 per cent. of the fat.

Plain Chocolate and Chocolate Powders.

The only differences that will be observed on analysis between chocolate or chocolate powders and cocoa powders are:

(1) A large proportion of sugar and some additional cacao butter in chocolate.

(2) The presence of sugar and probably foreign starches in chocolate powders.

The remaining components of cacao will be found in correspondingly decreased proportions.

Fat (22 per cent. to 30 per cent. of hard chocolate; 30 per cent. to 38 per cent. of "chocolat fondant"; 18 per cent. to 26 per cent. of chocolate powders).

The amount of fat in hard plain chocolates never exceeds 30 per cent. It has previously been pointed out that the fatty chocolates ("chocolats fondants") are much in vogue at the present time, and consist of ordinary cacao mass with sugar and a larger quantity of cacao butter than the hard

variety. "Chocolats fondants" are, moreover, refined to a greater degree than the older-fashioned hard chocolates.

The chemist should ascertain the nature of the fat extracted from the sample of chocolate, as there are many cacao butter substitutes on the market.*

In Chapter XVI, Table XXV, will be found analyses by Booth of some adulterated chocolates. The same author gives the following mean analysis (of twenty-four samples) of pure plain chocolates:

Fat, 27·4 per cent.; sugar, 53·4 per cent.; nitrogen, 0·93 per cent.; mineral matter, 1·32 per cent.; cold-water extract, 56·8 per cent.

Sugar (45 per cent. to 55 per cent. of plain chocolates; 50 per cent. to 60 per cent. of chocolate powders).

The amount of sugar added is, of course, optional to the manufacturer, though a quantity above 50 per cent. is difficult to work economically, as the chocolate is rendered less mobile and less easily moulded. A further addition of cacao butter, which is a costly ingredient, would have to be made, if the chocolate was not sufficiently fluid.

Sugar is the cheapening agent added to chocolate, and it is therefore to the advantage of the manufacturer to work in as much as possible.

In Switzerland a limit of 80 per cent. to 85 per cent. of fat and sugar together, the amount of sugar varying from 40 per cent. to 70 per cent. of the total chocolate, has been adopted as a standard.

Booth's recommendation that a legal standard for chocolate be adopted in England meets with our entire approval, though his limit for sugar suggested, namely, 65 per cent., seems to us too high.

The sugar added to chocolate should be the purest and driest cane- or beet-sugar.

* *Vide* Chapter XXIV, Table LIV.

Chocolate powders, used for drinking purposes, may contain larger quantities of sugar than plain eating chocolates, as the preparation is usually in a granular or powdery form. Booth suggests a limit of 75 per cent. of sugar for chocolate powders. This figure we also consider to be too high, seeing that starch is nearly always added, as well, in the preparation of chocolate powders for drinking purposes.

Starch.

The addition of starch to chocolate is not often met with, except in the cheapest preparations. As there is no legal standard for "chocolate" and its preparations in this country, there is nothing to prevent the use of starch, though chocolates prepared with it can readily be detected on the tongue, and are far from palatable.

At the present time a mixture of cocoa with sugar and starch cannot be sold as pure "cocoa," but only as "chocolate powder," and with a definite declaration that the article sold is a mixture of cocoa and other ingredients.

There are several highly nutritious cocoa preparations on the market, such as Epps's cocoa, prepared with selected arrowroot, starch, sugar and cocoa. There is no objection to such preparations as these, provided the public are fully aware what they are purchasing.

Cold-water Extract.

The cold-water extract, obtained from chocolate or chocolate powder, depends almost entirely upon the amount of sugar present.

This value is remarkably constant in the case of cacao nibs (approximately 24 per cent. of fat-free cacao), and a higher figure indicates the probable addition of sugar. The actual percentage of sugar is estimated by polarimetric

methods, the cold-water extract of pure cacao having a negligible power of rotating polarised light.

Milk Chocolates.

In Chapter XVIII will be found full analyses of milk chocolates by several chemists.

The average composition of milk chocolate is as follows:

Table LII.—*Composition of Milk Chocolates.*

	Booth.		Laxa.	
	English.	Continental.	I.	II.
Total fat	31·80	30·80	31·47	32·33
Milk fat	5·50	8·10	4·97	5·93
Cacao butter	26·30	22·70	26·50	26·40
Milk sugar	8·04	8·26	7·32	8·70
Cane or beet sugar . . .	43·20	42·60	27·51	35·93
Foreign starch	*Nil*	*Nil*	*Nil*	*Nil*
Cacao shell	*Nil*	*Nil*	*Nil*	*Nil*
Nitrogen	1·18	1·24	—	—

Laxa gives total proteid (I) 9·66 per cent.; (II) 8·13 per cent. The figures for milk fat and cacao butter are obtained by calculation (*vide* Chapter XVIII).

Fat (total :—30 per cent. to 35 per cent. of milk chocolate).

It will be seen that the fat is capable of division into milk fat and cacao butter, the total fat being somewhat in excess of that from ordinary plain, hard eating chocolates, and about equal to that obtained by extracting "chocolats fondants."

The chemical and physical constants of the fat, extracted from milk chocolate, will therefore vary according to the ratio of milk to cacao fat.

Milk Sugar (7·5 per cent. to 8·5 per cent. of milk chocolate).

It must be understood that the value for milk sugar will vary in the same way as the milk fat and nitrogen content of the chocolate, according to the amount of milk or milk solids added.

The copper-reducing power of plain chocolate is small, as the sugar added in the ordinary way will be cane- or beet-sugar, which, if pure, will have no reducing power, while that of cacao nibs does not amount to more than 5 parts per 100 of dry and fat-free cacao.

Milk sugar, on the other hand, has a strong copper-reducing power, and its presence can be inferred by the action of the cold-water extract upon a copper solution.

Nitrogen and Albuminoids.

The percentage of nitrogen and albuminoids or proteid matter will be greatly increased by the addition of milk solids to chocolate, the former increasing from 0·9 per cent. to 1·2 per cent. and the latter from about 5·5 per cent. to about 8·5 per cent.

The estimation of nitrogen is therefore a useful added factor in determining the amount of milk solids present in a milk chocolate.

CHAPTER XXIII

MICROSCOPICAL EXAMINATION OF CACAO AND ITS PREPARATIONS

Cacao Beans.

Through the courtesy of Mr. A. S. Bryden, of Barbadoes, I have been enabled to examine seeds of cacao fresh from the pod. The sample of cacao pod, which was undoubtedly of Forastero origin, arrived in an air-tight tin in remarkably good condition. The contents of the pigment-cells, which contained a certain amount of violet colouring matter on arrival, had probably undergone an oxidation process during transit, so that the beans on cutting showed a deeper violet coloration than would be expected when cut perfectly fresh.

Thin sections of the bean were examined in drops of vegetable oil, as a distinct cloudiness was noticed on placing the sections in water, due probably to the fat which the beans contained.

Starting from the outside covering of the beans, which were covered with a thick white slime of simple elongated cellular structure, the first and outer section of the shell of the bean was reached. The first epidermal layer consisted of a moderately thick skin containing polygonal cells, and lying directly beneath this were noticed the "exceedingly delicate transversely elongated cells," previously described by Ewell. The remainder of the shell consisted of closely compact bundles of spiral fibres, and a series of tissues

bearing thick-walled cells, which seemed to contain a large proportion of water. Within the shell was an exceedingly fine and transparent film or membrane, covering the whole of the kernel and falling into the spaces between the pieces or nibs of which the kernel is constructed.

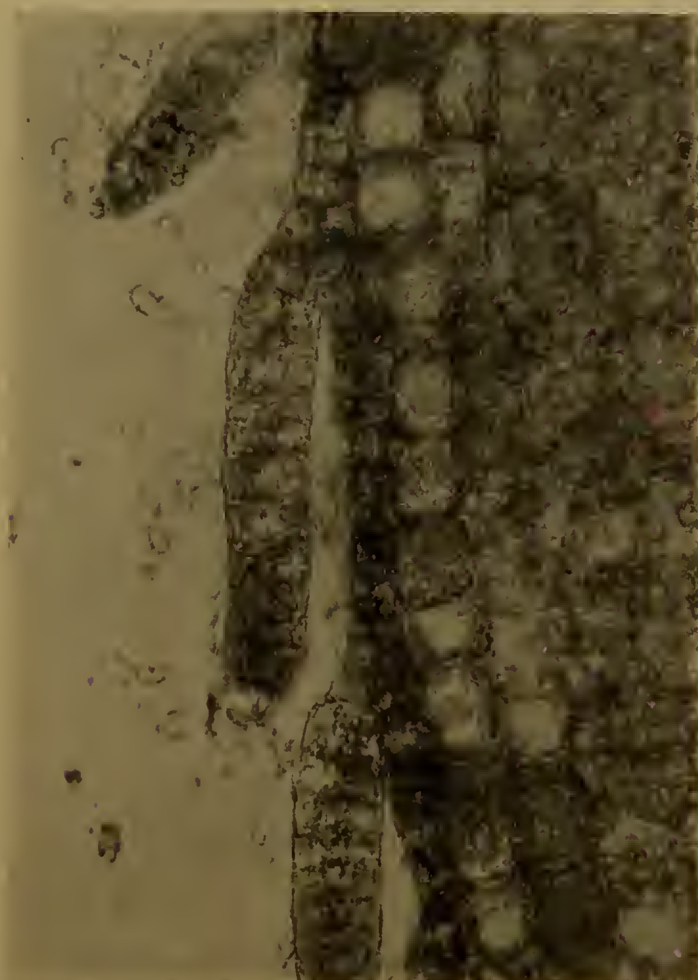
Upon this transparent film, which is made up of a

Photo, W. P. Paddison. *Brighton.*
FIG. 15.—"Mitscherlich" bodies between the lobes of the kernel. × 300 diam. (See p. 244.)

single layer of simple cells of irregular shape, the "Mitscherlich" bodies grow (Figs. 15 and 16). These bodies are "chrysalis-shaped," and were supposed by Hassall to be of fungoidal origin.

Hassall describes the thin membrane and the appearance of the "Mitscherlich" bodies in the following words: "Situated in the interspaces of the lobes is a fourth structure, attached externally to the second membrane, the cells

forming which pass down upon it for a short distance; although clear and transparent it exhibits a fibrous structure, and on its surface a considerable number of small crystals are always to be seen as well as many elongated bodies, rounded at their extremity and divided into several compartments or cells, and which do not appear to be



Photo, W. P. Paddison. *Brighton.*
FIG. 16.—"Mitscherlich" bodies enlarged. × 1000 diam. (See p. 244.)

attached to the membrane on which they lie. From their curious appearance and the absence of connection with any of the other structures of the cocoa seed the observer is led to suspect that they are extraneous and probably fungoidal growths. We have detected them in every sample of cocoa seed submitted to examination."

Had Hassall seen these bodies in fresh cacao beans, he

would have observed that they are attached to the thin membrane by an extremely small joint. It is probable that, during roasting and further treatment, the joint is broken, but that the bodies adhere to the thin membrane, as in all cases examined, after roasting, the bodies were found to be lying flat upon the membrane. The "Mitscherlich" bodies are now considered to be epidermal hairs, and though they are said to occur in every part of the seed, their origin is undoubtedly from the interlobe membrane.

In the fresh bean, the section of the cotyledon or kernel appears as closely packed polygonal cells filled with starch, fat, and albuminoid matters, whilst here and there the strongly violet-coloured pigment-cells show up prominently. The colour rapidly fades or dissipates, and it has been found impossible to preserve a specimen showing the pigment-cells with the colouring matter *in situ*.

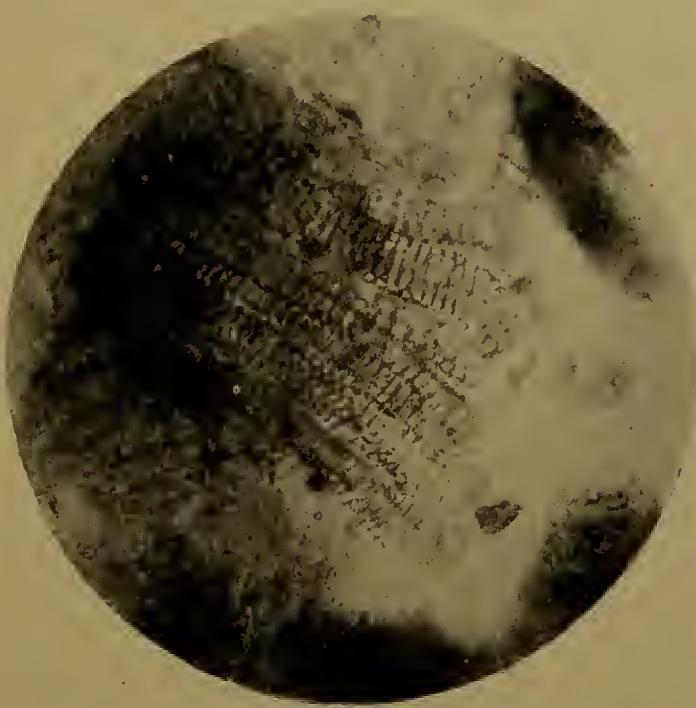
In the raw commercial and roasted kernel, the only real difference appears to be the change in the colouring matter, which permeates every cell, from violet to brown. The spiral bundles previously referred to as appearing in the shell are also to be found in the kernel, and are thrown into greater prominence by the processes of fermenting, curing and roasting, due to their being rendered opaque by loss of water (Fig. 17).

The starch granules occurring in cacao are very small, and are not likely to be confounded with any other variety which might be used for adulterating cacao preparations. They are estimated by Ewell to range from 0·003 mm. to 0·010 mm.

In preparing microscopic slides of cacao and its preparations, glycerine jelly will be found to be an excellent medium if the fat is not previously removed, and the cloudiness, already mentioned as appearing on placing the fat-containing body into water, has not been noticed. Crystals of theobromine may often be seen by using this

medium, though none were observed in sections taken from the fresh bean.

When using Canada balsam as a medium, the benzol that it contains, dissolves the fat, which, on slow setting of the medium, crystallises out as fine long needles. The benzol does not seemingly affect the theobromine crystals. It will be found desirable to defat the cacao and its preparations before making permanent slides in Canada balsam.



Photo, W. P. Paddison. *Brighton.*

FIG. 17.—Cocoa husk showing bundles of spirals. × 1000 diam. (See p. 246.)

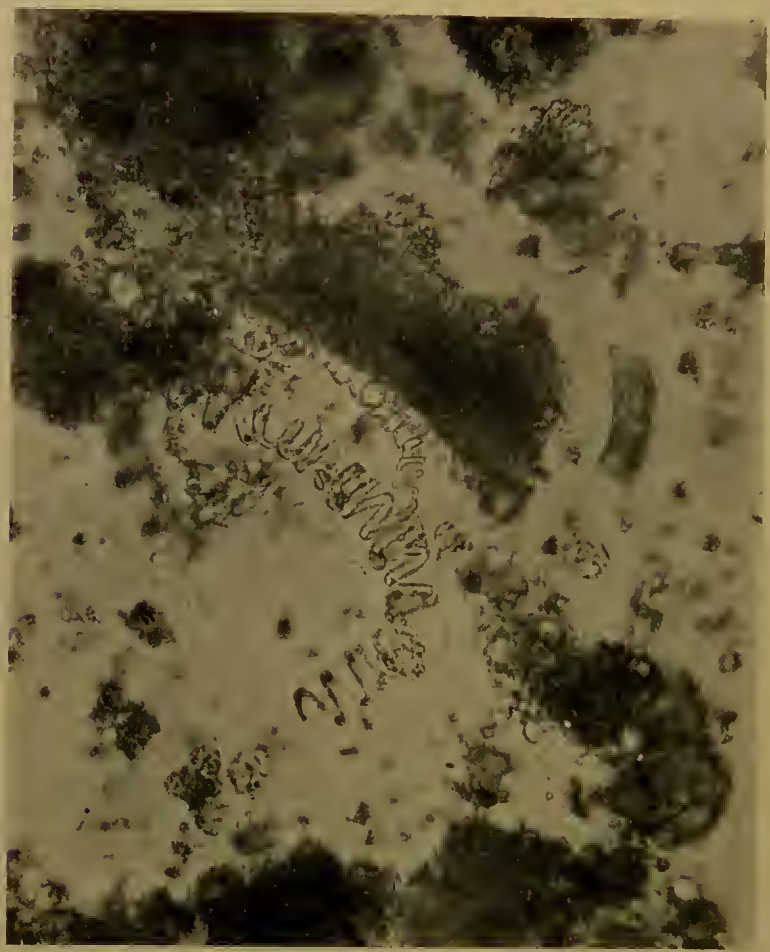
Mitscherlich has recommended the addition of petroleum ether as the means of differentiation between crystals of cacao fat and theobromine. There can, however, be no real confusion on this point, as the fat crystals are almost always the longer and more slender, and their appearance is not often observed, except on the thin transparent membrane, unless solvents are used to induce crystallisation.

The value of microscopic examination of cacao and its preparations lies largely in the detection of adulteration, and the close study of the structure of the bean, though of

great interest, is of little or no importance to the analytical chemist.

Cacao Preparations.

Pure cocoa powder should appear under the microscope



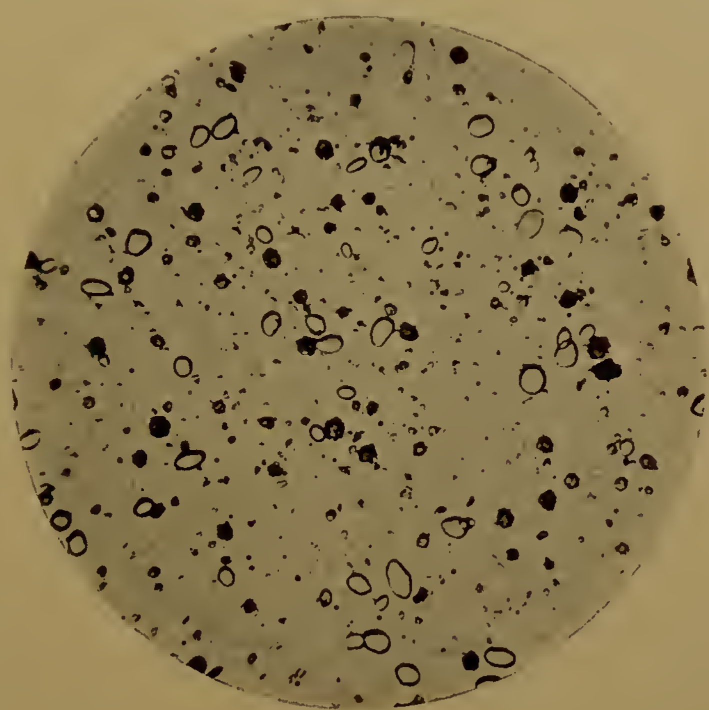
Photo, W. P. Paddison. *Brighton.*
Fig. 18.—Pure cocoa. × 1000 diam. (See p. 248.)

to contain no other ingredients than that of the cacao kernel (Fig. 18).

That is to say, pure cocoa powder will show cacao starch, the polygonal cells of the cacao kernel, traces of the transparent membrane covering the lobes of the kernel, and possibly the "Mitscherlich" bodies already described, and a certain quantity of isolated spirals. Pure cocoa powder should not show foreign starch, the characteristics of which are too well known to the microscopist to need description,

the sharp angular crystals of sugar, bundles of spirals typical of those appearing in the husk, rounded transparent crystals of sand, or any of the cellular tissues characteristic of the husk of cacao.

Foreign starch, sugar, and cacao husk constitute the principal adulterants of cocoa powders, and their presence can readily be detected under the microscope (Fig. 19), their quantity being determined by chemical means.



Photo, R. Whymper. *Ditton Hill.*

FIG. 19.—Cocoa adulterated with arrowroot starch. × 100 diam. (See p. 249.)

The proportions of added materials can only be approximated by means of the microscope.

To chocolate powders and eating chocolates the same remarks apply, though in the former case, the addition of foreign starch and sugar is not prohibited, and in the latter, sugar only is permissible. Earthy matters can also be detected under the microscope; it is, however, improbable that such adulterants as red ochre, venetian red, etc., mentioned by Hassall, will be met with, at the present day.

Further than this, the purity of the added starch, sugar, or other ingredients can often be determined, by examina-

tion under the microscope, and the fat, extracted from the preparation, can be examined independently if crystallised from ether, many of the fats with which cocoa and its preparations are likely to be adulterated having characteristic crystalline properties.

For further information regarding the microscopic structure of cacao, the valuable work of Moeler and Macé, 'Les substances alimentaires étudiées au microscope,' is recommended.

CHAPTER XXIV

METHODS OF ANALYSIS.—FAT.—DETERMINATION OF PHYSICAL AND CHEMICAL CONSTANTS OF CACAO BUTTER AND ITS SUBSTITUTES

The analysis of cacao beans consists essentially in determining the amount of moisture, fat, ash, fibre, nitrogen, and proteid matter that the nibs contain, the amount of husk obtained from the beans, and if an assay of husk is required, the amounts of moisture, fat, ash, nitrogen and proteid matter that are present.

An analysis of cocoa powder will require estimation of moisture, fat, ash, alkalinity of ash, fibre, nitrogen and proteid matter, cold-water extract, and pentosans.

A preliminary microscopic examination will reveal the presence of added starch and sugar, when, should either be present, a further estimation will be required.

A chocolate powder will require to be analysed for both added starch and sugar, besides the other components given under cocoa powders.

The analysis of a plain eating chocolate will necessitate determination of moisture, fat (cacao butter), ash, alkalinity of ash, nitrogen and proteid matter, cold-water extract, pentosans, and sugar.

Fancy chocolates may require further determinations, such as lactose or milk sugar, milk fat and casein in milk chocolates, vegetable oils in nut chocolates, etc.

All chocolates may contain added starch and cacao

butter substitutes, so that determination of the nature and quantity of both adulterants may be required.

Besides these estimations, those of theobromine, caffeine, cacao-red, etc., may be necessary if a close analysis is to be made.

The methods of analysis of the essential components of cacao and all its preparations will be described first.

In most cases more than one method will be given, that first described being recommended.

FAT.

The separation of cacao butter from cacao and its preparations has been the subject of considerable research. The net result obtained is that the quickest and most complete solvent is petroleum ether, which removes the cacao fat without any theobromine. Other solvents of cacao butter, such as carbon bisulphide, ether, and chloroform, remove a portion of the alkaloid also. Low fat results are invariably obtained if the cacao or its preparation is not reduced to an extremely fine powder, to which end the sample may be ground with previously extracted dry quartz sand, or the precautions recommended by Welmans* may be employed. In this method he suggests that, in the cases of chocolate and cacao mass and other fatty preparations, the sample be rubbed down in a mortar at 50° C. until the coarser particles are no longer visible. The fluid mass is allowed to solidify in tin moulds, and cooled; when cold the mass is rubbed on a grater and the whole operation repeated. By this method a fine homogeneous sample is obtained.

Method I.

5 grm. to 10 grm. of the finely divided sample are placed in a fat-free filter cone, and extracted with petroleum ether in a Soxhlet extractor. After the ether has passed over

* P. Welmans, 'Zeitsch. öffent. Chem.,' vi, 304.

from twelve to fifteen times, the flask, which had previously been weighed and which now contains the ether and fat, is subjected to gentle heat, and the ether distilled off. The flask, containing the fat, is then placed in the steam oven until no further loss in weight is observed, and the percentage of fat calculated.

Method II.

P. Welmans recommends the following procedure:

Five grms. of the finely divided powder are agitated in a separator with 100 c.c. of ether-saturated water till coherent particles are no longer observable; 100 c.c. of water, saturated with ether, are then added, and the mixture briskly agitated till an emulsion is formed.

The mixture is allowed to rest and separate into two layers. 25 c.c. to 50 c.c. of the clear ethereal solution on the top are removed by means of a pipette, the ether distilled off, and the residue weighed.

Method III.

A. Kreuz* makes use of chloral alcoholate as a solvent in the following method:

2 grm. to 3 grm. of the sample and 3 grm. of chloral alcoholate, are placed in a flask and heated to a homogeneous mass. To this mixture 15 c.c. of ether are added, and the contents of the flask well shaken; a further 35 c.c. of ether are added, and the whole filtered into a weighed flask. The residue in the filter is washed twice with pure ether. The flask and ethereal solution of fat is dried at 105° to 110° C., at which temperature the chloral alcoholate is completely expelled.

In a subsequent communication he recommends the removal of the chloral alcoholate by heating under reduced pressure at a temperature of about 75° C. The residue so

* A. Kreuz, 'Zeitsch. Nahr. Genussm.,' 1908, xv, 680, and xvi, 584.

obtained is treated with chloroform to re-dissolve the fat, the solution filtered to separate the theobromine and cacao-red, the filtrate evaporated, and the fat weighed.

Method IV.

Davies and McLellan,* and Steinmann,† recommend the use of rectified petroleum ether boiling at 60° C. as the solvent, the latter author pointing out the errors caused by making use of Kreuz's method (III) to be considerable, especially in the case of chocolates.

The Soxhlet method is recommended by these observers.

The use of ethyl alcohol for obtaining a finely divided sample for subsequent extraction is recommended by many observers.‡

After the quantitative extraction of a small carefully weighed sample of cacao or its preparation, a larger quantity must be extracted for the qualitative tests to be performed upon the fat.

The high price of cacao butter has caused the frequent substitution of other vegetable fats, and though not prohibited in this country, owing to the lack of legal standardisation, it is certainly desirable to ascertain the nature of the fat employed.

The substitutes of cacao butter which are most likely to be encountered are given, with their constants, in Table LIV. There are, however, a number of qualitative tests which can be rapidly performed, and which afford a useful indication as to the purity of the cacao butter before the more elaborate methods of estimating its constants need be used. The most important of these is the Björklund's ether test.

* S. H. Davies and B. G. McLellan, 'Journ. Soc. Chem. Ind.,' 1904, 480.

† A. Steinmann, 'Chem. Zeit.,' 1905, xxix, 1074.

‡ Tschaplowitz, 'Zeitsch. anal. Chem.,' 1906, xlv, 231; A. Kirschner, 'Zeitsch. Nahr. Genussm.,' 1906, xi, 450, etc.

Björklund's Ether Test.

The ether test, which, in a modified form, constitutes the British Pharmacopœia test of purity, consists in shaking a quantity of the fat (3 grm.) in a test-tube with twice its weight of ether at 18° C. Pure cacao butter produces a clear solution, whilst the presence of wax will at once cause turbidity, which will not clear even on warming.

If a clear solution is obtained, the test-tube is immersed in water at 0° C., and the minutes which elapse before turbity occurs noted.

Björklund made the following observations:

	Turbidity at 0° C. after minutes.	Clear solution at degrees C.
Pure cacao butter . . .	10–15 .	19–20
Cacao butter + 15 per cent. beef tallow	8 .	22
Cocao butter + 10 per cent. beef tallow . . .	7 .	25

It has been observed also that the form of the crystals in the chilled ethereal solution is a useful indication of the addition of tallow, pure cacao butter crystallising in well-defined shapes at the bottom and sides of the tube, whilst a small percentage of tallow renders the solution cloudy and flocculent.

Refractive Index on Zeiss Butyro-Refractometer.

The determination of the refractive index of a fat has long been known as a useful indication for the state of purity.

The instrument in general use is the Zeiss butyro-refractometer, which, from its handiness and for general utility, is most to be recommended.

There are a few oils, however, such as tung oil and the resin oils, which fall without the scale (5° to 105° on the

butyrometer), and for these the Abbé refractometer, or the oleo-refractometer of Amagat and Jean, may be used.

The Zeiss butyro-refractometer which consists of an Abbé double prism, capable of being heated by a current of hot water, and a permanently attached telescope, the objective of which is adjusted by a micrometer screw, does not need further description, the method of working being one of greatest simplicity.

Some figures of value for the detection of adulteration of cacao butter obtained by the author are given:

	Readings on Zeiss butyro-refractometer at 40° C.
Cacao butter	46–47
Coconut stearin	35–36
Beef tallow	48·5–49·0
Palm butter (hard)	47·0
Palm-kernel oil	38–39
Earth-nut oil	55–56
Butter fat	42–45 (usually 44·5)
Hazel-nut oil	54·2
Almond oil	57·2
Fat from Cailler's milk chocolate	46·0
do. Nestlé's do.	46·0
do. Peter's do.	46·2
do. "Nuttis" (Peek Frean's Nut chocolate)	50·0

It has been thought desirable to include for consideration only those physical and chemical constants of cacao butter which are of the greatest importance and value to the analyst, and which will enable him to detect the presence and extent of adulteration with foreign fats. For this purpose the methods of estimation of the specific gravity, the melting-point, the melting-point of the fatty acids, the saponification value, the Reichert-Meissl value, and the iodine value only will be discussed. If further information

concerning the estimation of other values for cacao butter is required, Allen's 'Commercial Organic Analysis,' vol. ii, 1910, is to be recommended.

In the works of Alder Wright, Lewkowitsch and others on oils, fats, waxes, etc., will also be found full descriptive details for the processes involved in estimating acid value, Hehner value, acetyl value, bromine value, refractive index, etc., which may be required from time to time for special cases.

Specific Gravity.

The specific gravity of a fat is largely dependent on its constitution. The determination of this value, therefore, is of some importance in detecting adulteration of cacao butter with any particular oil or fat.

In the case of an oil, the determination of specific gravity can be made by means of a hydrometer, specific gravity bottle, or Sprengel tube at any moderate temperature and compared against that of water at 15·5° C., which in England is usually taken as the unit of comparison.

In the case of a fat or wax solid at ordinary temperatures, such as cacao butter, the fat is melted and the specific gravity taken at some higher temperature, preferably the boiling-point of water (100° C.).

The Sprengel tube, which gives more accurate results than the hydrometer or specific gravity bottle, is constructed of thin glass tubing, having an internal diameter of about $\frac{1}{2}$ in. The tube is usually bent into a U-shape, terminating at both ends in capillary tubing.

The weight of the Sprengel tube and of the volume of water it contains at 15·5° C. is first ascertained. The clean dry tube is then filled with the molten fat by immersing one end of the capillary tube in the liquid, and applying suction to the other. The whole is then placed in a beaker

of boiling water in such a way that only the extreme tips of the capillaries are not covered.

As the temperature of the molten fat rises expansion occurs, and the oil drips from the fine orifices of the capillary. As soon as expansion has ceased and the oil has attained the temperature of the boiling water, the Sprengel tube is removed, carefully dried, cooled and weighed.

The weight of the contents divided by the weight of water which the tube originally contained at 15·5° C. will give the specific gravity of the oil at 100° C. compared with water at 15·5° C.

Table LIII shows the specific gravities of various fats, solid at the ordinary temperatures, as observed by Allen. Though these results were obtained by a different method (the Plummet method*), they could have been ascertained by the Sprengel tube method described with equal facility and greater accuracy.

TABLE LIII.—*Specific Gravities of Cacao Butter and some possible Adulterants.*

	Sp. gr. of melted fats, etc. : Water at 15·5° C (1,000).		Difference for 1° C.
Cacao butter	892·1 at 50° C.	857·7 at 98° C.	0·717
Palm oil	893·0 at 50°	858·6 at 98°	0·717
Japan wax	901·8 at 60°	875·5 at 98°	0·692
Tallow	895·0 at 50°	862·6 at 98°	0·673
Butter fat	904·1 at 40°	867·7 at 99°	0·617
Coconut stearin	895·9 at 60°	869·6 at 99°	0·674
Coconut oil	911·5 at 40°	873·6 at 99°	0·642
Palm nut oil	911·9 at 40°	873·1 at 99°	0·657
Paraffin wax	780·5 at 60°	753·0 at 98°	0·724

The specific gravity of a fat may vary within narrow limits according to the method of expression or extraction, the presence of fatty acids, the age of the oil, and other circumstances.

* *Vide* Allen's 'Commercial Organic Analysis,' 1910, ii, 48.

Melting and Solidifying Points.

The addition of extremely small quantities of oil will rapidly lower both the melting point and the solidifying point of cacao butter. The reverse is the case on addition of a fat or wax of higher melting point.

The true melting point of cacao butter lies between 30° and 34° C., when it fuses to a transparent yellow liquid, which congeals again at 20·5° C.

Melting Point—Method I.

The cacao fat is first melted at about 33° C. and drawn up into a fine thin capillary tube, made by drawing out a piece of ordinary quill tubing. The fat is made to solidify immediately in the tube, and it is then placed away for two or three hours. The longer the fat is allowed to remain solidified up to, say, twenty-four hours, the more nearly will the true melting point of the fat be obtained. The capillary tube, which is open at both ends, is attached to an accurate thermometer at its bulb by a thin piece of rubber band or tubing.

The thermometer and attached tube are then immersed in water, which is *very gradually* heated and constantly stirred until fusion of the fat takes place. The mean of the temperatures at the point of fusion of the fat observed over a number of experiments may be taken as the melting point.

The flame is then removed from beneath the receptacle containing the water, and the temperature at which the fat solidifies observed as the water cools.

As a rule the solidifying point of a fat is at a very much lower temperature than the melting point—this is the case with cacao butter.

Method II.

The method of determining the melting point of fats adopted by the A.O.A.C. is somewhat more complicated, though extremely accurate.

The fat, melted and filtered, is made to fall from a dropping tube, from a height of 15 to 20 cm., on to a smooth piece of ice floating in distilled water.

The discs of solid fat so formed (1 to 1·5 cm. in diameter) weigh about 200 mgrm., and are removed by pressing the ice under the water, when they float to the surface, and can be readily removed.

The apparatus employed consists of a boiling tube, 35 cm. long and 10 cm. diameter, containing a smaller test-tube, 30 cm. long and 3·5 cm. diameter. A small-bulbed thermometer and fittings for blowing air into the outer tube complete the apparatus.

Some distilled water and 95 per cent. alcohol are first separately boiled to remove any traces of air which they might contain in solution.

The hot water is then poured into the inner tube until the latter is half full, when the hot alcohol is admitted slowly down the side until the tube is about three-quarters filled.

The object of these precautions is, firstly, to prevent the formation of bubbles of air on the disc of fat, which is subsequently placed in the inner tube, and secondly, to avoid complete mixing of the alcohol and water. The inner tube is then placed in the boiling tube containing ice-cold water until the contents of the former are quite cold.

When cold, the disc of fat is placed in the inner tube containing the alcohol and water, into which the disc sinks, until the specific gravity of the mixture is the same as that of the fat.

The delicate thermometer with a fine bulb is let down into the inner tube so that the bulb is just above the disc.

The temperature of the water in the boiling tube is now gently raised, and the water kept constantly stirred by blowing in air from a rubber blowing bulb to the bottom of the boiling tube.

When the temperature has been raised within a few degrees of the melting point of the fat, the disc of fat will be seen to shrivel, and at this point the thermometer should be lowered so that the level of the bulb is the same as that of the disc, and a gentle stirring motion given, to cause a uniform temperature in the neighbourhood of the disc.

As soon as the fat disc has assumed a practically spherical shape, the temperature of the solution in which it is immersed is taken at the level of the disc.

A second and third repetition of this operation will give very accurate readings for the melting point of the fat.

Solidifying Point.

The determination of the solidifying point of the fats is of comparatively little importance, and may be made after the determination of the melting point described under Method I. It is desirable, however, to substitute a capillary tube closed at one end for that open at both ends, as used in this method.

The value of estimating the melting and solidifying points of the fatty acids obtained from the fats is considerable, and the variations occurring in the figures of the two estimations are less than when the natural fats are employed.

Method I.

A modification of Dalican's method, official in the United States, is extremely accurate, and embodies the original method suggested by Dalican, with the precaution of constant quantities of chemicals for the preparation of the fatty acids, standard dimensions of apparatus, etc., so that the solidifying point of the fatty acids can be determined under strictly comparable conditions.

25 grm. of fat are saponified with 60 c.c. of 30 per cent. sodium hydroxide solution (36° B.) and 75 c.c of 95 per cent.

alcohol, or 120 c.c. of water, in a platinum dish, and the mass evaporated to dryness.

The dried soap is dissolved by 1000 c.c. of boiling water, and the solution boiled until all the alcohol has been expelled (usually about forty minutes). The solution is then treated with 100 c.c. of 30 per cent. sulphuric acid (25° B.), and heated until the fatty acids set free are quite clear.

The fatty acids are then thoroughly washed with fresh quantities of distilled water, separated in a separating funnel, filtered through a dry filter-paper, and thoroughly dried for twenty to thirty minutes in a steam-heated oven at 100° C.

The dried fatty acids are allowed to cool to 15° or 20° C. above the suspected melting point; they are then poured into a test-tube 100 mm. long and 25 mm. in diameter.

This test-tube is made to fit into an empty flask, 150 mm. long by 70 mm. in diameter, by means of a cork, and a thermometer registering from 10° to 60° C., and graduated in tenths of a degree, is passed through a hole in a cork of the inner tube until the bulb reaches the middle of the material. The 10° mark on the scale of the thermometer should be about 3 cm. above the bulb, and the entire length of the thermometer should not exceed 36 cm.

When the fat or fatty acids commence to solidify at the bottom of the tube or around the sides, the thermometer should be given a gentle stirring motion to equalise the temperature of the material. At first the temperature will be seen to fall slowly, and then to rise to a point when the mercury will remain stationary for one to two minutes.

The readings of the thermometer should be taken at short and equal intervals of time, and the highest temperature recorded during the short rise following the fall of the mercury gives the solidifying point or "titer" of the material.

The experiment should be repeated two or three times, and the readings obtained should not vary more than 0·1° C. if proper care has been exercised.

Other Methods.

There are several other well-recognised methods of determining the solidifying point of fatty acids, etc.

Finkener's* method, which has an official status in Germany for the differentiation of lard, tallow and candle fats, Wolfbauer's† method, Shukoff's‡ method, and others, can be found described in Allen's 'Commercial Organic Analysis,' 1910, ii, 56–58, or in the original papers given in the foot-notes.

It has been found that the method and duration of saponification have no material influence on the results obtained by any of the foregoing methods, the most important factors in obtaining consistent results being the complete expulsion of alcohol after saponification and the thorough drying of the fatty acids.

For the methods of determining other physical constants of cacao butter such as action on polarised light, electrical conductivity, viscosity, heat of combination, etc., Allen's 'Commercial Organic Analysis,' vol. ii, Lewkowitsch's and Alder Wright's books on oils, fats, waxes, etc., should be consulted.

Saponification Value or Koettstorfer§ Value.

The saponification value of an oil or fat is expressed as the number of milligrammes of potassium hydroxide required for the complete saponification of 1 gramme of that oil or fat.

Oils and fats of the nature which will come under the notice of the chocolate manufacturer and his chemist, are,

* Finkener, 'Chem. Zeit.,' 1896, xx, 132.

† Wolfbauer, 'Mitl. techn. Gew. Mus. in Wien.,' 1894, 57.

‡ Shukoff, 'Chem. Zeit.,' 1901, xxv, 1111.

§ Koettstorfer, 'Zeitsch. anal. Chem.,' 1879, xviii, 199.

with the exception of paraffin wax, broken up by the action of alcoholic alkali into the alkaline salt or soap of the fatty acids existing in the fat, and glycerol or glycerin which existed originally in the fat as the glyceride or glycerol compound of the fatty acids.

The saponification of fatty oils is a perfectly definite reaction, and not only can the proportion of fatty acid and glycerol produced from any fat or glyceride be determined, but the actual amount of alkali involved in the reaction can be ascertained. Thus in the general equation—

$$C_3H_5A + 3\ KOH \longrightarrow C_3H_5(OH)_3 + 3\ KA,$$

the fat or glyceride (C_3H_5A), containing a fatty acid A, combines with potassium hydroxide (KOH) to give glycerol ($C_3H_5[OH]_3$) and the potassium salt or soap of the fatty acid A (KA).

In the above equation the number of parts of fat saponified by 1 molecule of potassium hydroxide will be one third of its molecular weight, but in the case of an ester of a monatomic alcohol the number will be identical to its molecular weight. This figure is briefly what is termed the "saponification equivalent," and represents the amount of oil or fat in grammes which would be saponified by 1000 c.c. of a normal solution (N) of any alkali.

In determining the saponification value, however, the amount of fat is the constant, and the amount of alkali is the variable.

Method I.

From 1·2 to 2 grm. of the fat are weighed out and treated with an accurately measured 25 c.c. of approximately semi-normal ($\frac{N}{2}$) solution of potassium hydroxide in alcohol, in a flask bearing a long tube to act as an air-condenser.

The alcohol should be previously freed from water by keeping an excess of dry potassium carbonate in the bottle containing it.

The flask and its contents are heated on a water bath until solution of the fat has taken place and the saponification is complete. This usually takes from thirty to forty-five minutes.

In order to ensure greater accuracy in the subsequent titration a test experiment should be conducted side by side with the fat undergoing saponification.

The test experiment consists of measuring out accurately 25 c.c. of the same approximately $\frac{N}{2}$ potassium hydroxide solution previously added to the fat, and heating it in a similarly constructed flask to that in which the fat is being saponified for the same length of time.

One c.c. of a 1 per cent. alcoholic solution of phenolphthalein is then added to each flask, and the liquids titrated with $\frac{N}{2}$ hydrochloric acid.

The difference between the volumes of standard acid used in the two cases will give the number of cubic centimetres corresponding to the alkali neutralised in saponifying the oil, each cubic centimetre of $\frac{N}{2}$ hydrochloric acid (18·25 grm. of hydrochloric acid in 1000 c.c. of solution) representing 0·02805 grm. of potassium hydroxide (KOH). From these figures the number of milligrammes of potassium hydroxide required to saponify 1 grm. of the fat can readily be obtained.

From the saponification value so found the saponification equivalent can be calculated by dividing the former into 561, and multiplying the result by 100.

Method II.

A method of cold saponification may at times be found useful.

In this method, 3 to 4 grm. of the fat dissolved in 25

c.c. of re-distilled petroleum ether are treated with 25 c.c. of normal (N) alcoholic potassium hydroxide solution, and the mixture after thorough shaking is kept in a flask for twenty-four hours. The excess of alkali is titrated with standard hydrochloric acid as previously described. A blank experiment must be conducted side by side with the fat undergoing saponification, in order to check the strength of the alcoholic potassium hydroxide employed, and which will vary from day to day.

Reichert-Meissl Value.

The Reichert-Meissl value, which is of special importance in butter analysis, is a modification by Meissl* of Reichert's† method for the estimation of the number of cubic centimetres of decinormal $(\frac{N}{10})$ alkali solution required to neutralise the distillate obtained from an acidified solution of a fat previously saponified under definite conditions. Reichert's original method need not be discussed here, but will be found, if required, in the paper mentioned in the foot-note.

Method I.

5 grm. of the fat are carefully weighed out and cautiously heated, with constant shaking, over a small flame in a 300 c.c. Erlenmeyer flask with 20 c.c. of glycerol (specific gravity, 1·26) and 2 c.c. of sodium hydroxide solution (100 grm. sodium hydroxide in 100 c.c. of water).

The water is then evaporated off, an operation which usually takes five to eight minutes and results in the formation of a clear liquid.

The flask and contents are warmed over a steam- or water-bath until the fat is completely saponified. It is

* Meissl, 'Dinglers Polyt.,' 1879, ccxxxiii, 229.

† Reichert, 'Zeitsch. anal. Chem.,' 1879, xviii, 68.

then allowed to cool to about 80° C. and treated with 90 c.c. of distilled water at the same temperature.

The solution is then acidified with 50 c.c. of dilute sulphuric acid (50 c.c. of strong acid in 1000 c.c. of water), and the volatile fatty acids set free are distilled off.

Before distillation, care should be taken that the fatty acids are quite molten and that the globules in the emulsion have fused together. This may be brought about by heating the flask and contents on the water bath until the fatty acids appear as a transparent oily layer on the surface of the water.

Distillation.

After the fatty acids have separated into a clear layer on the surface of the water, the flask is cooled to the temperature of the room, and a few pieces of pumice-stone added. The pumice-stone should be prepared by heating it to a white heat and throwing it into distilled water, in which it is kept immersed until wanted.

The flask is now connected to a glass condenser, and slowly heated over a naked flame until the contents commence to boil. After this the flame is so regulated that 110 c.c. of distillate passes over it in thirty minutes, the rate of the distillation being kept as near as possible to these figures. The distillate should be received into a flask accurately marked at 110 c.c.

Titration of the Volatile Fatty Acids.

The 110 c.c. of distillate, after thorough shaking, are filtered through a dry filter-paper; 100 c.c. of the clear filtrate are then measured into a flask of about 250 c.c. capacity, and 0·5 c.c. of phenolphthalein solution (1 grm. in 100 c.c. of alcohol) added.

$\frac{N}{10}$ barium hydroxide solution is run into the fatty acids

until the red coloration, which remains permanently for two or three minutes, is produced. The number of c.c. of $\frac{N}{10}$ barium hydroxide solution required should be increased by one tenth, in order to allow for the 10 c.c. of acid distillate not used.

Other Methods.

The method described is essentially that devised by Leffman and Beam* and based on the Reichert-Meissl method.

Other methods official in various countries are similar in the main points to Method I.

Wollny,† in order to obviate errors arising from absorption of carbon dioxide, from variation in the size, shape and nature of the apparatus, and from the differing strengths of solutions employed, has made certain conditions under which the estimation should be made.

This has been adopted in its essential features by the A.O.A.C.

Iodine Value.

The principle underlying the iodine and bromine values of fats and oils has already been given in Chapter XX, and the determination of the amount of iodine or bromine fixed by a given acid or mixture of acids affords useful information as to the nature of the fatty acids present.

The absorption of free iodine by fats and oils is slower than the absorption of bromine, but the following methods described will be found to give accurate and consistent results in the shortest possible time.

* Leffman and Beam, 'The Analyst,' 1891, xvi, 153; 1896, xxi, 251.

† Wollny, 'The Analyst,' 1887, xii, 203, and 'Milch Zeit.,' 1887, Nos. 32–35.

Method I.

The first method, which was devised by Hübl,* is as follows:

Solutions required.

1. An alcoholic solution of mercuric chloride is prepared by dissolving 60 grm. of corrosive sublimate or mercuric chloride in 1 litre of 95 per cent. alcohol. The solution is filtered and placed in a well-stoppered bottle.

2. An alcoholic solution of iodine is prepared by dissolving 50 grm. of iodine in 1 litre of 95 per cent. alcohol.

3. Sodium thiosulphate solution (about 24 grm. to the litre) standardised against pure sublimed iodine or potassium bichromate.

Before determining the iodine values of fats or oils, equal volumes of the first two solutions are taken and thoroughly mixed in a well-stoppered bottle, where they should be allowed to remain for at least twenty-four hours in order that any iodine-consuming impurities may be eliminated.

From 0·8 to 1·0 grm. of a solid fat, such as cacao butter, or up to 0·5 grm. of drying or non-drying oils, is weighed out and dissolved in 10 c.c. of pure chloroform, which should not contain any iodine-consuming impurity.

To the chloroform solution is added 30 to 40 c.c. of the mixed iodine and mercuric chloride solution, more being introduced if on standing for two to three hours the brown-coloured mixture lightens in colour to any extent.

A large excess of free iodine, about equal to the amount absorbed, should remain in the solution undergoing the treatment, after the fat has fixed all the iodine of which it is capable.

The mixed solution should be allowed to remain in

* Hübl, 'Dinglers Polyt.,' 1884, ccliii, 284.

close-stoppered bottles in the dark for several hours, preferably from twelve to twenty-four hours, when the iodine absorption should be complete.

When the process is complete, from 10 to 15 c.c. of a 10 per cent. solution of potassium iodide are added, with about 150 c.c. of water, and the excess of iodine present titrated with the standardised solution of sodium thiosulphate, a little starch paste being used as indicator towards the end of the titration.

The difference between the iodine found in the blank and real determination will give the amount of iodine absorbed, which, calculated on 100 grm. of fat, will give the iodine value required.

As the mixed solution of iodine and mercuric chloride varies in strength from day to day, and the chloroform may contain certain quantities of iodine-consuming impurities, it is most necessary to carry out a blank experiment side by side with the actual determination. The same quantities of solution and the same operations as were involved in the actual determination should be employed for the blank experiment, with the exception that in the latter case no fat is added.

The iodine value is always estimated as the amount of iodine absorbed by 100 parts of fat.

The actual products formed during the Hübl process of estimating the iodine value have been the matter for considerable discussion.

From the researches of Hübl, Ephraim,* Wijs,† Lewkowitsch,‡ and others, it would appear conclusive that during the mixing of the iodine and mercuric chloride solutions a certain proportion of mercuric iodide is formed with, possibly, a small quantity of iodine monochloride.

* Ephraim, 'Zeitsch. angew. Chem.,' 1895, 254.

† Wijs, *ibid.*, 1898, 291.

‡ Lewkowitsch, 'The Analyst,' 1899, xxiv, 257.

It is probable, therefore, that the fatty halogen compound eventually formed is not a simple iodine addition product but one containing both iodine and chlorine.

Method II.

A method suggested by Wijs has considerably lessened the time taken for absorption, by making use of the action of water on iodine chloride to form hypoiodous acid, which he considers to be the chief agent in accelerating the absorption.

The iodine chloride Wijs prepared by dissolving 13 grm. of iodine in a litre of glacial acetic acid, and introducing chlorine until the amount of thiosulphate required by the solution was doubled. With a little practice the correct point can be detected by the change in colour of the solution. The solution so prepared is practically an acetic acid solution of iodine chloride, and is fairly stable. This solution is used in the same way as Hübl's mixed solutions, with the advantage that the time of absorption is greatly reduced.

Other Methods.

Other methods have been devised by Welmans* and Waller,† and can be found in the original papers given in the foot-notes, or in the works on oils, fats and waxes by Lewkowitsch and Wright.

CACAO BUTTER SUBSTITUTES: SPECIAL TESTS.

In Table LIV will be found physical and chemical constants for cacao butter, and for those fats and oils with which it is likely to be adulterated. There are also included in the same table constants for those fats and oils which

* Welmans, 'Journ. Soc. Chem. Ind.,' 1900, xix, 694.

† Waller, 'The Analyst,' 1895, xx, 280.

may be found in conjunction with cacao butter in the fat extracted by a solvent from commercial chocolates other than plain, such as milk, nut, and other chocolates.

The determination of fat constants, the values for which are dependent upon the composition of the fat, affords some indication of the nature and extent of adulteration. Thus a high iodine value suggests the presence of certain foreign vegetable oils, such as sesame, arachis or almond. A low saponification value will suggest beeswax or paraffin wax. A low iodine value will be found if coconut oil or stearin has been substituted for cacao butter.

In general the vegetable oils increase the iodine absorption value and lower the melting point of the insoluble fatty acids obtained from the mixed fats.

Cacao butter may show a high acid value if the fat has been extracted from shells (Dutch Ha butter) or unduly exposed to the oxidising influence of air and light. The acid value given by Matthes and Rohdlich* for cacao butter is 1·1 to 1·95.

There have been many researches upon the detection of cacao butter substitutes in chocolate. Coconut fat or stearin, after a great part of the olein has been removed, is especially suitable as a cacao butter substitute. Wauters† suggests the following method for the detection of coconut fat in cacao butter:

Five grammes of the extracted fat (if from chocolate) is saponified and the soap dissolved in 150 c.c. of boiling water; 50 c.c. of 5 per cent. sulphuric acid solution are then added and the whole is distilled so that 100 c.c. pass over in thirty to thirty-five minutes. After the first distillation another 100 c.c. of water are added and the distillation repeated. The two distillates are separately filtered, and 50 c.c. of each filtrate titrated against a $\frac{N}{10}$

* Matthes and Rohdlich, 'Ber.,' 1908.

† Wauters, 'The Analyst,' 1901, xxvi, 128 and 292.

solution of caustic soda. The filters are washed with 50 c.c. of ethyl alcohol, and the washings mixed with the 50 c.c. of the filtrate, and again titrated.

By this method, which is really an extension of that for estimation of the Reichert-Meissl value, Wauters obtained the following results, the figures being expressed as cubic centimetres of $\frac{N}{10}$ caustic soda solution required for neutralisation:

	Soluble volatile acids.			Insoluble volatile acids.		
	1st.	2nd.	Total.	1st.	2nd.	Total.
Coconut oil	7·1	4·3	11·4	7·85	7·55	15·4
Cacao butter	0·1	—	0·1	0·25	0·15	0·4

Sachs* has examined many exotic vegetable fats which have been used as substitutes for cacao butter. Dika or Gaboon fat, Tankawang fat or Borneo tallow and Illipé fat have been examined by this author, who gives also the constants he obtained for them.

The same author has examined the stearin obtained from coconut and palm nut fats. He suggests the admixture of 75 per cent. coconut stearin with 25 per cent. Japan wax for a good cacao butter substitute. This mixture gives the following constants: Melting-point 34° to 35·5° C.; iodine value, 7·8; saponification value, 237; Reichert-Meissl value, 5·5.

Other mixtures recommended by Sachs are two thirds palm nut stearin with one third coconut stearin, and 40 per cent. Tankawang fat with 60 per cent. coconut stearin.

* O. Sachs, 'The Analyst,' 1908, 123.

Table LIV.—*Physical and Chemical Constants of Cacao Butter, etc.*

Fat, or oil.	Specific gravity. At °C.	M.P. °C.	M.P. of fatty acids. °C.	Saponification value.	Reichert-Meissl value.	Iodine value.
Cacao butter .	0·964–0·974 at 15° 0·8577 at 98°	30–34	48–53	192–195	0·2–0·9	32–42
Possible adulterants :						
Bassia tallow . (Mixture of Mohwah and Mahua butters) . .	0·9175 at 15° 0·8943–0·8961 at 100°	25–42	39·5–45	187–194	0·5–0·8	54–68
Borneo tallow .	0·892 at 100°	37·5	53·5	192·4–196	0·3–0·5	30–31
Chinese tallow .	0·9180–0·9217 at 15°	36–46	39–57	179–203	0·2	23–38
Cotton seed stearin	0·867 at 100°	30–40	27–45	194·5	0·8–1·0	89–93
Goa butter . (Kokum butter)	0·911 at 50° 0·8889 at 100°	41–43	61·0	187–191 5	0·1–1·5	25–34
Mafura tallow .	0·902 at 40°/15°	29–40	51–55	201–221	1·5	43·5–56
Nutmeg butter .	0·945–0·996 at 15°	43-51	42·5	154–161	1–4·2	48–85
Palm oil . .	0·9210–0·9245 at 15°	27–43	48–50	200–205	0·8–1·9	53–58
Phulwara butter (Karité fat)	0·8970 at 100°/100°	39	—	191	0·4	42
Piney tallow . (Malabar tallow)	0·915 at 15° 0·8900 at 100°	36–42	56	189–191	0·2–0·4	38–39
Shea butter . (Galam butter)	0·9175 at 15° 0·859 at 99·5/15·5°	23–28	39·5–56	179–192	—	56–67
Coconut oil .	0·9259 at 15° 0·8736 at 100°	20–28	24–25	246–262	6·6–8·4	8·2–9·5
Coconut stearin .	0·8700 at 100°	29·3–29 5	28·1	252	3·4	4·0–4·5
Palm nut . (Palm kernel oil) .	0·8731 at 99°/15°5	23–30	21–28·5	243–255	5–6·8	10·5–17·5
Palm nut stearin .	0·8700 at 100°	31·5–32	28·5–29·5	242	2·2	8
Beef fat . .	0·8950 at 15·5° 0·8626 at 98°–100°	42–50	41–47·5	196	0·3–0·5	36–42
Lard . . .	0·8600 at 98°–100°	30–44	37–47	195–203	0·2	47·5–64
Mutton fat . .	0·937–0·953 at 15·5°	47–49	34–36	196	0·3	33–50
Tallow . . .	0·925–0·940 at 15·5°	38–50	41–49	193–198	0·2	33·48
Beeswax (normal)	0·959–0·970 0·962–0·966 at 15·5°	62–66	—	88–98*	—	8·5–11·5
Paraffin wax . .	0·824–0·940 at 15·5° (according to melting-point)	36·7–58·3	—	—	—	3·9–4 0
Possibly present, due to addition of nuts, milk, etc.:		Solidification point.				
Almond oil . .	0·914–0·920 at 15·5°	–10 to –20°	13–14	188–192	0·5	93–100
Arachis (Earth nut) oil	0·911–0·926 at 15·5°	+ 3 to + 10	27–30	186–194	0·5	83–101
Hazelnut oil . .	0·916–0·917 at 15·5°	–10 to –20	20–25	191–197	0·9–1·0	83–90
Pine-nut oil . .	0·9215–0·9250 at 15·5°	–18 to –20	16–19	191–193	—	106–120
Walnut oil . .	0·9240–0·9268 at 15·5°	–12 to –24	15–20	190–197	0·9	139–148
		Melting-point.				
Butter fat . .	0·909–0·913 at 38·5°	28–36	38–42	215·8–241·1	21 0–33·4	28–42

CHAPTER XXV

METHODS OF ANALYSIS: MOISTURE—MINERAL MATTER (SOLUBLE, INSOLUBLE, ALKALINITY OF)—COLD WATER EXTRACT—FIBRE (CRUDE FIBRE, CELLULOSE, PENTOSANS)—CACAO-RED—XANTHINE BASES (THEOBROMINE, CAFFEINE) — ORGANIC ACIDS (TARTARIC, ACETIC, OXALIC)

Moisture.

The estimation of moisture is of only minor importance to the analyst, though it is desirable for the manufacturer to keep this value as low as possible, seeing that mouldiness and general deterioration of quality result from excess of moisture in cacao and its preparations.

Method.

From 2 to 5 grm. of the powdered sample are distributed evenly over the bottom of a platinum dish previously heated, cooled and weighed. The dish and its contents are placed in a steam-heated oven and maintained at 100° C. until, after frequent weighings, no further loss in weight occurs. The loss in weight may be attributed to water lost at 100° C., the quantity of theobromine and other volatile matters which escape at this temperature being negligible.

Mineral Matter or Ash.

Method.

The quantity of sample previously employed for moisture determination is incinerated firstly over a naked gas flame until the fat and other easily combustible matter

is thoroughly charred, and then in a muffle furnace until no further loss in weight occurs. The residue represents the mineral matter or ash.

If no addition of foreign mineral matter in the form of husk, alkali, etc., has been made, the amount of ash found is a direct indication of the quantity of cocoa matter present in the sample.

(a) Soluble and Insoluble Ash. Method.

About 20 to 30 c.c. of distilled water are added to the mineral matter in a platinum dish, and the water brought to the boil. The solution is then filtered through a clean filter-paper, and the residue thoroughly washed with repeated small quantities of hot water until the filtrate amounts to about 80 c.c. The filtrate is evaporated in a clean weighed platinum dish, and heated in a muffle furnace. The increase in weight will be the soluble ash.

The filter-paper and residue are dried in a steam oven and incinerated in a second platinum dish previously weighed. The increase in weight, after allowing for the amount of ash contained in the filter-paper (usually about 0·001 per cent.), will be the insoluble ash.

The amount of insoluble is always higher than the soluble ash in pure cacao mass, being usually about 66 per cent. against 33 per cent. of the total ash respectively. The roasted germ shows a higher soluble ash, Bordas finding 57 per cent. against 43 per cent. of insoluble ash. The same author gives the figures reversed for roasted shells, namely, 43 per cent. for soluble and 57 per cent. for insoluble ash.

Stutzer* has shown in a clear manner how the soluble ash is increased by the addition of alkaline carbonates to cacao preparations. He states that the ash from pure cacao preparations does not effervesce with dilute mineral acids, and

* A. Stutzer, 'Zeitsch. angew. Chem.,' 1892, 510.

is soluble in water to the extent of one third of its total weight.

Booth* points out the importance of determining the ratio of soluble to total ash as confirmatory evidence of the addition of ochre and other mineral colouring matter. If the soluble ash is more than half that of the total, the addition of husk or added alkali is probable.

(*b*) *Ash or Mineral Matter insoluble in Acid. Method.*

2 grm. of the sample are incinerated as previously described, and boiled with 25 c.c. of 10 per cent. hydrochloric acid solution for five minutes.

The insoluble matter is collected and estimated by filtering the solution through a Gooch crucible, washing the residue with hot water, igniting and weighing. The residue obtained in this manner is almost entirely composed of silica. The estimation of the ash insoluble in mineral acids may be of considerable value, as the figure is considerably higher in the husk than in the nibs of cacao.

(*c*) *Alkalinity of the Ash.*

The official method of determining alkalinity of ash adopted by the A.O.A.C.† is as follows :

Method.

The entire ash obtained by incinerating 2 gr. of the sample is treated with excess of $\frac{N}{10}$ hydrochloric acid solution (usually from 10 to 15 c.c.) in a platinum dish.

The solution is brought to the boiling-point by heating the platinum dish and contents over a Bunsen flame. The solution is then cooled, and the excess of hydrochloric acid titrated with $\frac{N}{10}$ sodium hydroxide solution. The

* N. P. Booth, 'The Analyst,' 1909, xxxiv, 141.

† U.S. Dept. of Agriculture, 1907, Bull. 107.

alkalinity is expressed as the number of c.c. of $\frac{N}{10}$ sodium hydroxide to neutralise the ash obtained from 1 grm. of the sample.

In this work the alkalinity has been always expressed as potassium oxide (K_2O), this being the method adopted by modern chemists.

It is evident that the addition of fixed alkalis in the preparation of cocoa or chocolate will lead to the increased alkalinity of the ash found.

Bordas has given figures showing the increase in potassium estimated as oxide (K_2O) found, by the addition of potassium carbonate or hydroxide, in certain commercial cocoas examined. His results are tabulated below:

Kind of cocoa.	Salts of potassium in 100 parts of dry, defatted cocoa. As K_2O.	As K_2CO_3.
Ordinary cocoas (mean)	2·54	3·87
Cocoa treated with alkali I	4·82	7·07
,, ,, ,, II	4·86	7·12
,, ,, ,, III	5·02	7·36
,, ,, ,, IV	6·41	9·41
,, ,, ,, V	5·74	8·42

Bordas states that the addition of potassium salts renders the cocoas strongly alkaline, whilst ordinary cocoas are slightly acid in reaction.

Farnsteiner has pointed out that, if the ash obtained from 100 grm. of a sample of cocoa requires more than 15 c.c. of N acid for its neutralisation, and at the same time the ash insoluble in water is more than 60 per cent. of the total ash, the sample has been treated with magnesium carbonate.

The same author states that the addition of ammonium carbonate can be detected by heating the cocoa with water and magnesium oxide in a flask, in the neck of which is

suspended a piece of faintly red litmus paper. The ammonia liberated by this treatment will turn the red litmus paper blue.

The quantity of ammonia present can be estimated by distilling into a standard $\frac{N}{10}$ acid solution and titrating the excess of acid remaining.

Cold Water Extract: Cocoa Matter Soluble and Insoluble in Cold Water.

The amount of matter soluble in cold water is, according to Booth, about 24 per cent. of the fat-free nib. Bordas, however, gives 9·67 per cent. for the same figure.

We have obtained figures ranging from 9 per cent. to 12·5 per cent. for the whole nib, results which are in accordance with those obtained by the first author.

The addition of sugar, alkaline salts, etc., will considerably affect this value. Thus in chocolate the cold water extract may rise to 70 per cent.

Bordas makes use of the matter insoluble in cold water for estimating the amount of defatting that a cocoa has undergone. Booth uses the cold water extract for estimating the amount of cocoa matter present in a sample on the assumption that cocoa nibs contain 12 per cent. of soluble extractive.*

Method.

A simple method for the estimation of the cold water extract is as follows:

2 grm. of the sample are placed in a 100 c.c. flask, and shaken with 50 to 60 c.c. of water. The solution is then made up to 100 c.c. and left standing overnight. 25 c.c. of this solution are filtered off, evaporated, dried and weighed.

* *Vide* Chapter XXVI.

More rapid and consistent results will be obtained if the material is defatted before extracting.

Fibre.

The determination of fibre, though simple in itself, is not readily interpreted.

Firstly, the complex nature of fibre makes it difficult to say what is precisely obtained by any given treatment, and secondly, the word "fibre" conveys to the mind the cellulose tissue of plant life, while it is not cellulose alone which has been estimated when the value for fibre is given.

From the most recent researches it has been shown that the cell-walls of plant life are composed for the most part of compounds of sugars (of the hexoses and pentoses). The outer cellular structure of seeds contains cellulose and these same sugar compounds intermingled with various organic bodies, colouring matters, tannin, etc.

The estimation of crude fibre therefore may be the estimation of cellulose or a mixture of cellulose and other bodies, according to the treatment to which the material is subjected.

The amount of crude fibre found is greater in the outer shells or husks than in the kernel or nibs of cacao, and whether it is the direct estimation of the "crude fibre" of Filsinger, the determination of the cellulose of Weender, or the indirect estimation of fibre by determination of the pentosan content of the cacao as carried out by Tollens and his pupils, or by König, the values obtained are a clear indication of the extent of adulteration of cacao preparations with husk.

Method I.

Weender's process modified by König for estimating the amount of crude fibre (chiefly as cellulose) consists

in treating 3 grm. of the defatted sample with 200 c.c. of glycerol (S.G. 1·23), containing 4 grm. of concentrated sulphuric acid, under a pressure of 3 atmospheres for one hour. The solution is then filtered whilst hot through an asbestos filter, washed successively with hot water, alcohol and ether, and the residue dried and weighed.

The residue is then incinerated, and the ash weighed. The difference between the two weighings gives the amount of ash-free crude fibre present in the sample.

Method II.

An alternative method for the estimation of crude fibre is as follows:

2 grm. of the sample are freed from fat by extraction with ether, and the residue boiled for half an hour under a reflux condenser with 200 c.c. of water and 2·5 c.c. of sulphuric acid. The liquid is filtered through linen, and the residue after filtration is thoroughly washed with hot water, and subsequently boiled with 200 c.c. of 1·25 per cent. caustic soda solution. The residue undissolved is filtered off, washed successively with hot water, alcohol, and ether, dried at 100° C. and weighed.

In cocoa free from husk the value for crude fibre obtained in this manner will amount to 2 per cent. or 3 per cent., but will exceed this limit in proportion to the amount of husk present.

Method III.—Direct Estimation of Husk.

As the determination of crude fibre is practically a measure of the amount of husk present in a cocoa, Goske's* method of direct estimation of husk, based upon the difference between the specific gravity of cocoa husk and that of ordinary cocoa powder, should be mentioned here.

* A. Goske, 'Zeitsch. Nahr. Genussm.,' 1910, xix, 154.

Dubois and Lott* have recently studied this method, and state it to be of only approximate accuracy.

Goske recommends that 1 grm. of dry fat-free cocoa be mixed with a calcium chloride solution (of specific gravity = 1·535 at 30° C. prepared by dissolving 107·1 grm. of calcium chloride in 100 c.c. of water) in a stoppered tube. After thorough shaking, the stopper of the tube is removed, and the whole boiled for two minutes. While still hot the tube is submitted to centrifugal action for six minutes.

The top liquid portion is poured off, and the sediment collected on a weighed filter-paper, washed well with hot water until the filtrate is free from chlorine, dried and weighed.

On the assumption that cacao husk yields 38·7 per cent. of dried sediment, this being the maximum figure found for husk, and that commercial cocoa powders yield 6 per cent., the percentage of added husk in a cocoa powder can be readily calculated. Allowance must be made for the fat removed.

An example given is that of a sample of cocoa, 1 grm. of which gave 0·0618 grm. of sediment. Using the figure 38·7, this amount is equivalent to 0·16 grm. of husk. The cocoa powder contained 18·4 per cent. of fat, hence an amount equivalent to 13 per cent. of husk was originally present. Allowing for the 6 per cent. contained by normal cocoa powders, the sample contained 7 per cent. of added husk.

(a) *Cellulose.—Method of Estimation.*

From 1 to 5 grm. of sample are boiled with a dilute mineral acid, in order to render the starch completely soluble. The solution is filtered, and the residue thoroughly washed with hot water, and subsequently warmed with

* Dubois and Lott, 'Journ. Ind. Eng. Chem.,' 1911, iii, 251.

a 1 per cent. solution of soda. The solution is filtered and the residue washed successively with water and alcohol, dried at 100° C. and weighed. The weight found, after a deduction has been made for any mineral matter which the residue might contain, may be considered to be cellulose, and is a fairly constant quantity, amounting to about 4·9 per 100 parts of pure cacao mass, or 14·9 for 100 parts of cocoa matter insoluble in water.

Any addition of husk, germ, or cacao waste tends to increase the cellulose and to decrease the starch content of the cocoa.

(*b*) *Pentosans.*

As already described in a previous chapter, the fibrous material comprising the cell-walls of plants is composed chiefly of anhydrides of pentoses or sugars containing C_5. These anhydrides are called pentosans, and yield on hydrolysis a pentose sugar xylose, arabinose, etc.

The quantitative determination of xylose and arabinose by themselves is comparatively simple, but in the vegetable kingdom these sugars are in a condensed form, and associated with hexoses and other sugars which complicate their direct determination.

It becomes necessary, therefore, to determine the pentosans present by the indirect methods of estimating the products which are formed from them by chemical action, and which are characteristic of the pentoses and not of the other sugars with which they may be associated.

Tollens and his pupils have been largely instrumental in perfecting processes by which the pentosans may be estimated, and which rest mainly on the quantitative determination of furfurol, a decomposition product which is formed by heating the pentoses with dilute hydrochloric acid. The chemical explanation, which is really merely one of abstraction of water, is explained by the equation :

$$C_5H_{10}O_5 \longrightarrow 3\ H_2O + C_5H_4O_2.$$

Method I.

This method, which has been used with success by Hehner and Sketchley,* Adan,† and others, and suggested by Tollens in conjunction with Gunther and de Chalmont, has been shown to have an efficiency of from 99·1 per cent. to 101·1 per cent. over a range of experiments carried out by Adan :

3 to 4 grm. of the sample are placed in a Wurtz flask of 250 c.c. capacity, with 100 c.c. of dilute hydrochloric acid of 1·06 specific gravity (equivalent to 12 per cent. HCl). The contents are then distilled until 30 c.c. have passed over, when 30 c.c. of dilute acid are let in to the flask to take the place of that portion which has distilled over. This process is continued until about 300 c.c. of distillate have been collected. As the distillation proceeds the furfurol can be detected by allowing a drop of the distillate to fall on a filter-paper, which is then tested with a drop of dilute aniline acetate solution, containing a small proportion of sodium acetate. When a pink coloration is no longer produced the distillation is stopped.

The distillate is made up to 400 c.c. with dilute hydrochloric acid (specific gravity 1·06).

The solution is then slowly neutralised with dry and finely powdered sodium carbonate, and then faintly acidified with acetic acid; 10 c.c. or more if required of an acetic acid solution of phenylhydrazine (12 drops of phenylhydrazine to 7·5 c.c. of strong acetic acid) are added, and the solution constantly stirred.

The volume is then increased to 500 c.c. with constant stirring for half an hour. The precipitate is collected on an asbestos filter, washed thoroughly and quickly with water and dried in a current of warm air (50° to 60° C.) under slightly reduced pressure.

* O. Hehner and N. P. Sketchley, 'The Analyst,' 1899, xxiv, 178.

† R. Adan, 'Bull. Soc. Chim. Belg.,' xxi, 211.

The weight of precipitate multiplied by 0·516 will give the weight of precipitated or distilled furfurol.

An error of about 0·25 per cent. may occur if the amount of furfurol remaining in the solution and washings has not been included.

Method II.

This method, suggested by Councler, has been used by König with success, and is similar in operation to *Method I* up to the end of the distillation of the furfurol.

The 400 c.c. of acid distillate is treated with a solution of pure phloroglucinol in dilute hydrochloric acid, and the mixture allowed to stand over-night. The precipitate is then collected on an asbestos filter, thoroughly washed and dried just below 100° C. for several hours till no further loss in weight occurs.

An efficiency of 99·5 per cent. to 101·2 per cent. was obtained by this method by Adan.

From Tollens' data the amount of furfurol can be calculated after the following corrections have been made :

1 grm. furfurol produces 1·82 grm. phloroglucide for 0·1 grm. precipitated furfurol.

1 grm. furfurol produces 1·92 grm. phloroglucide for 0·2 grm. precipitated furfurol.

1 grm. furfurol produces 1·93 grm. phloroglucide for 0·3–0·5 grm. precipitated furfurol, and by means of interpolation the intermediate figures can be calculated.

From the furfurol so found a value 0·0104 is subtracted, and the remainder multiplied by 1·88 or its correction will give the equivalent of pentosan.

The percentage of pentosan can thus be readily calculated.

As has already been stated the results of this method show a satisfactory efficiency when pure furfurol has been used for test purposes, and has been recommended by the

Committee of the International Congress of Applied Chemistry (1909) as an excellent criterion of the purity of cocoa powders with regard to their freedom from husk.

Cacao-red.

The pigment of cacao is an oxidation product of tannin, and is not apparent in the fresh beans.

By the action of light and air, the cacao-red is developed in much the same way as the colouring matter of the oak and kola nut. The original pigment compounds have been shown to decrease during fermentation (*vide* Chapter V, Table II), as also do the astringent matters.

During oxidation of the seed Schweitzer * has shown that a glucoside, cacaonin, is decomposed by a diastatic ferment with the production of sugar and cacao-red. The pigment obtained in this way is of a complex nature and consists of tannin and resin, besides the red-brown amorphous colouring matter to which the name of "phlobaphene" has been given.

The pure cacao-red is only of scientific interest, and the estimation of the colouring matter of cacao is seldom required.

Method.

From 2 to 3 grm. of fat-free cocoa are made into a paste with hydrochloric acid, and exhausted with 100 c.c. of absolute alcohol in a Soxhlet tube. The hydrochloric acid is fixed by placing in the flask below some silver oxide, so that any acid extracted with the alcohol is converted into insoluble silver chloride.

The alcoholic liquid, after cooling and filtering, is treated with alcoholic lead acetate solution, when a purple black precipitate is formed.

* C. Schweitzer, 'Pharm. Zeit.,' 1898, 389.

The precipitate is collected on a filter-paper, washed well with hot water, and transferred to a small flask with a small quantity of 70 per cent. alcohol.

The lead salt in suspension is then decomposed by sulphuretted hydrogen, the solution warmed to get rid of the sulphuretted hydrogen, and then filtered. The lead sulphide will remain as residue, whilst an alcoholic solution of cacao-red passes through as filtrate.

From the alcoholic solution the pigment can be obtained as a solid by evaporation, and, after drying, weighed.

An alcoholic solution of cacao red when viewed through a spectroscope gives a diffuse band in the green, allowing the red, blue, and most of the yellow rays to be transmitted.*

Xanthine Bases (Theobromine and Caffeine).

The determinations of the alkaloids of cacao are of importance, principally due to the fact that cacao preparations owe their stimulating property to their presence.

The methods recommended for the estimation of the alkaloids are numerous, and unfortunately do not give consistent results.

The majority of the methods suggested are untrustworthy, especially those which rely upon the estimation of theobromine by sublimation. The most systematic results have been obtained by employing the methods described by Kunze† and Dekker,‡ a modified combination of the two methods being recommended by the A.O.A.C.

Method I (Kunze's Method).

10 grm. of the sample are boiled for twenty minutes with 100 c.c. of 5 per cent. sulphuric acid. The solution

* Blyth, 'Foods, their Composition and Analysis,' 1909, 369.

† W. E. Kunze, 'Zeitsch. anal. Chem.,' 1894, xxxiii, 1.

‡ J. Dekker, 'Rec. Trav. Chim.,' 1903, xxii, 143.

is filtered and the residue thoroughly washed with boiling water.

The warm filtrate is precipitated with excess of phospho-molybdic acid, and after twenty-four hours' standing the precipitate is collected on a filter-paper, and washed with about one litre of 5 per cent. sulphuric acid.

The filter containing the moist precipitate is transferred to a large dish, and treated with excess of cold baryta, after which carbon dioxide is passed in to precipitate the barium hydroxide.

The whole is then dried on a water bath, and extracted with chloroform.

The chloroform is distilled off from the clear filtered extract, when a perfectly white deposit of the two alkaloids, theobromine and caffeine, is left.

The white residue is weighed, dissolved in ammonia, and heating to boiling point. Excess of silver nitrate is then added (11·3 parts of silver to 1 part of theobromine), and the boiling continued until no further ammonia escapes and the liquid is reduced to a few cubic centimetres.

An insoluble substitution product of theobromine ($C_7H_7AgN_4O_2$) is obtained, while the caffeine remains uncombined in solution.

The insoluble precipitate is filtered off, washed, and weighed.

The silver is estimated in the dried theobromine silver compound by ignition or by dissolving in nitric acid and precipitating as chloride.

By either of these means the quantity of theobromine, in combination with the silver and originally present, can be readily determined.

The difference between the weight of theobromine found and the total alkaloids will give the amount of caffeine present.

Method II (Dekker's Method).

This process, which has greater brevity in its favour, is capable of giving very accurate results.

10 grm. of the powdered sample are heated with 5 grm. of magnesium oxide and 300 c.c. of water in a reflux condenser for one hour.

After filtering and draining on a pump, the residue is again boiled with water for fifteen minutes, and drained.

The mixed solutions are evaporated to dryness, and the resulting residue triturated with fine sand, and boiled with 100 c.c. of chloroform.

The clear chloroform solution is filtered and evaporated to dryness, and the white residue, consisting of theobromine and caffeine, weighed. If it is desired to estimate the two alkaloids separately, the dried residue is treated with 50 c.c. of benzol for twenty-four hours, by which means the caffeine is dissolved. The solution is evaporated to a volume of 25 c.c. and filtered. The residue, consisting of theobromine, is dried and weighed.

By this process Dekker obtained results varying from 1·69 per cent. to 1·73 per cent. of mixed alkaloids in cocoa.

Welmans* has obtained satisfactory results by a slight modification of Dekker's method, and Fromme† has verified the accuracy of the process. Katz‡ has also experimented with the method and has obtained consistent results.

Maupy,§ by a slightly different process, obtained results agreeing with Dekker's figures, namely, 1·3 per cent. to 1·6 per cent. of mixed alkaloids in roasted nibs, and 0·54 per cent. in chocolate containing 60 per cent. of sugar.

Kreutz,‖ by yet another method, has succeeded in ob-

* P. Welmans, 'Pharm. Zeit.,' 1902, xlvii, 858.

† J. Fromme, 'Apoth. Zeit.,' 1904, xviii, 68.

‡ Katz, 'Chem. Zeit.,' 1903, xxvii, 958.

§ L. Maupy, 'Journ. Pharm. Chim.,' 1897, v, 329

‖ A. Kreutz, 'Zeitsch. Nahr. Genussm.,' 1908, xvi, 579.

taining consistent results, though in all cases his figures are somewhat higher than those obtained by Kunze's and Dekker's methods. Kreutz finds total alkaloids from 1·99 per cent. to 3·85 per cent. in the nibs, 1·99 per cent. to 2·23 per cent. in Van Houten's cocoa, and 2·63 per cent. to 2·92 per cent. in Suchard's cocoa.

The reason for the inconsistency among the results obtained is owing largely to the fact that a portion of the theobromine is combined as a glucoside and is not set free without treatment with an acid or other hydrolysing agent. Kreutz found that only half of the total theobromine is immediately capable of extraction by chloroform, the remainder becoming soluble only after the glucoside had been hydrolysed.

Organic Acids (Acetic, Tartaric, and Oxalic Acids).

Schweitzer* has pointed out that the plant acids, malic and tartaric acids, occurring in cacao are due to the decomposition of the glucoside cacaonin, which, under the action of a ferment, breaks up into sugar, and malic and tartaric acids.

On referring to Chapter V, Table II, it will be seen that a loss of both free and combined tartaric acid occurs during the processes of fermentation and curing of the beans, and that an increase in free acetic acid is noted.

Professor Harrison, who conducted the latter research, has systematically studied the chemistry of cacao from the fresh beans through the various operations which render them fit for the market, and his results are not only rational but consistent over a number of experiments. It is to be doubted whether Schweitzer has fully proved the accuracy of his statement, or if the production of tartaric acid by the hydrolysis of the glucoside is sufficiently large to be taken into account.

* C. Schweitzer, 'Pharm. Zeit.,' 1898, 390.

The increase in acetic acid during fermentation is incontestable, due to the fact that the alcohol formed during the first period is converted by *Mycoderma aceti* into acetic acid, which can be detected in the cured commercial beans by the vinegar-like smell, as well as by chemical analysis.

The determinations of tartaric and acetic acids are not of commercial importance, and the total acidity of an aqueous extract of cacao nibs estimated in terms of K_2O does not exceed 0·75 per cent.

Tartaric Acid (Weigmann's Method).

From 5 to 10 grm. of the sample are treated with 50 c.c. of water and thoroughly shaken. The aqueous extract is neutralised with ammonia, and treated with calcium chloride solution.

The precipitate is filtered and dissolved in hydrochloric acid, and then reprecipitated with caustic soda solution.

By this method Leffman and Beam* found from 4·34 per cent. to 5·82 per cent. of tartaric acid to be present in cacao. These we consider to be very high figures, for the total tartaric acid found by us has not exceeded 1 per cent.

Oxalic Acid.

The older experimenters on cacao do not include oxalic acid among the constituents, though the presence of oxalic acid in vegetable matters has been recognised for a considerable time.

Gautier has given values of 0·375 per cent. oxalic acid in black tea, 0·013 per cent. in coffee, and 0·247 per cent. in stick rhubarb. The same author has found 0·45 per cent. of oxalic acid in cocoa powder.

A certain amount of interest is attached to the estima-

* Leffman and Beam, 'Food Analysis,' 1901, 275-282.

tion of oxalic acid in that Albahary* has found that the acid is present mainly as insoluble calcium oxalate in ordinary cocoa powder, whilst treatment with alkali in the preparation of "soluble" cocoa powder brings about the decomposition of the calcium oxalate with the production of soluble alkaline oxalate.

In two samples of cocoa powder marked N and P respectively, the former treated with alkali and the latter an ordinary cocoa powder, Albahary obtained 0·3459 per cent. of oxalic acid combined as soluble alkali out of a total of 0·3647 per cent. in sample N, and only 0·0159 per cent. of soluble oxalate in sample P with 0·3763 per cent. combined with calcium.

The researches of Neubauer,† Schultzen,‡ Salkowski§ and others on the estimation of oxalic acid in cacao and its preparations have been carefully examined by Albahary, who has proposed the adoption of the following method:

Method.

About 50 grm. of the sample, dried over sulphuric acid until of constant weight, are placed in a beaker with 50 c.c. of a 10 per cent. sodium carbonate solution.

The beaker and contents are heated on a water bath for one hour, the liquor evaporating being replaced by an equal amount of water.

To the solution is then added 50 c.c. of a solution containing 10 parts of magnesium chloride and 20 parts ammonium chloride to the 100 c.c.

A small quantity of animal black is added and the liquid stirred whilst the solution continues to concentrate on the water bath.

* J. M. Albahary, 'Internat. Cong. App. Chem.,' 1909, viiiC, 175.
† Neubauer, 'Zeitsch. anal. Chem.,' 1868, ii, 499, and vii, 225.
‡ Schultzen, 'Reichert und Dubois Reymond's Arch.,' 1868, 718.
§ Salkowski, 'Zeitsch. phys. Chem.,' x, 120.

After an hour, and when the volume has been reduced by about one half, the solution is filtered on a pump without allowing it to get cold, and the insoluble residue thoroughly washed with boiling water until the filtrate is quite neutral.

The filtrate is again concentrated on the water bath, and after the addition of enough ammonia to render the solution strongly alkaline, the beaker and contents are left to cool for twelve hours.

The solution is then filtered, and a slight excess of calcium chloride solution and enough acetic acid to render the solution faintly acid are added. The solution is again left to stand for twelve hours.

All the calcium oxalate is thrown down in this manner, and, after collecting the precipitate on a filter, the oxalic acid is estimated by igniting the dried residue, weighing the oxide of calcium so formed, and calculating the oxalic acid that it represents.

Girard, who has recently carried out researches on the oxalic acid content of cacao and its preparation, has given some valuable figures, a few of which have been shown in Chapter XXI, Table XLVII.

CHAPTER XXVI

METHODS OF ANALYSIS: REDUCING MATTERS, TOTAL NITROGEN AND ALBUMINOIDS, STARCH, CANE SUGAR AND MILK SUGAR, CACAO MATTER

In this chapter the analyses of the ingredients added to cacao in the preparation of chocolate, and themselves present in the nibs to a small extent, will be described.

Apart from the possible additions of cacao butter and alkali, which have already been dealt with, a plain chocolate will contain sugar. Starch may also be found to be present in cocoa and chocolate powders and eating chocolates, though in all cases it should be looked upon as an adulterant.

In milk chocolates, the addition of the solids of milk will increase the reducing matters due to the presence of milk sugar or lactose, as well as the nitrogenous matters due to the casein which milk contains.

By the addition of the milk solids of full-cream milk a new fat, butter fat, is also introduced, which further complicates analysis.

The direct estimation of cacao matter present in a preparation is not possible by chemical means, and as this value is of great importance owing to the regulations and standards of purity existing in many countries, and to the fact that a rebate may be obtained on the amount of cacao matter exported which has paid duty on entering this country, both the manufacturer and chemist should be in a position to state how much cacao matter any preparation contains.

To this end the characteristic qualities of cacao mass and of its components have been observed, so that an estimation of one or several of the components, by direct or indirect means, may be converted into terms of cacao matter present.

Reducing Matters.

The reducing power of a substance is the extent to which that substance is capable of reducing a standard solution of copper with the precipitation of cuprous oxide.

Certain sugars, such as glucose, lactose, etc., possess reducing power, and if the conditions of strength of solutions, temperature and time, are kept constant throughout, a given weight of the sugar will precipitate a uniform quantity of cuprous oxide (estimated as cupric oxide) constant for that sugar.

The average reducing power of 100 grm. of dry fat-free cacao is about five parts of cupric oxide. The addition therefore of even small quantities of soluble reducing matters will greatly increase the reducing power of the cold water extract of the cacao preparation.

The reducing matters of pure cacao will include the small quantities of glucose, etc., which, as has been shown in former chapters (*vide* Chapters V and VIII, Tables II and V), are present in the original beans.

Method I (by Fehling's Solution).

The standard solution of copper is made up as follows: 34·5 grm. of copper sulphate are dissolved in 450 c.c. of water and the solution accurately made up to 500 c.c.

173 grm. of Rochelle salt (sodium-potassium tartrate) and 63 grm. of anhydrous sodium hydrate are dissolved in water and the solution made up to 500 c.c.

The two solutions should be kept separate, but for use equal volumes of the two solutions are taken.

A very slight reduction takes place on heating the two solutions (about 3 mgrm. of cupric oxide for every 50 c.c. of the mixed solutions), and should be estimated if great accuracy is required.

The reducing matter to be measured should be so regulated that from 150 to 350 mgrm. of cupric oxide are precipitated.

50 c.c. of the mixed Fehling's solution are placed in a wide-mouthed flask of 250 c.c. capacity, and immersed in boiling water until the temperature of the solution is stationary.

An accurately weighed or measured solution of the reducing matters is then added, and the whole made up to 100 c.c. with boiling distilled water.

The heating is continued for exactly twelve minutes, when the solution is filtered through a double filter-paper, and the residue of cuprous oxide thoroughly washed and dried.

The cuprous oxide is converted into cupric oxide by slowly charring the filter-papers and contents, and heating the residue in a weighed porcelain dish, first to a dull red, then to a bright red heat, in a muffle furnace or over a Bunsen flame.

The cupric oxide may then be weighed direct, converted into copper by reducing with hydrogen, or, after dissolving the oxide in nitric acid, may be deposited as copper electrolytically.

Method II (by Pavy's Solution).

The copper solution is prepared by dissolving 20·4 grm. of Rochelle salt and 20·4 grm. of caustic potash in 200 c.c. of water. In another 200 c.c. of water 4·158 grm. of copper sulphate are dissolved. The two solutions are then mixed, and when cold 300 c.c. of strong ammonia (S.G. 0·880) are added, and the whole made up to 1000 c.c. with water.

The solution is standardised against a known weight of inverted cane sugar, when it will be found that 10 c.c. of Pavy's solution, prepared as above, diluted to 20 c.c. with water, equals about 5 mgrm. of glucose.

Estimations with this solution are made as follows: 10 c.c. of Pavy's solution are placed in a wide-mouthed flask and an equal bulk of water added. A rubber stopper with two holes is fitted into the flask; into one hole is tightly placed the tapering end of a burette, whilst into the other is fitted a long glass tube, preferably extending to the open air, to carry away the ammonia fumes.

The burette is now filled with the solution containing the reducing matters, and the flask containing Pavy's solution brought to the boiling point.

The stopcock of the burette is opened and a small quantity of the solution run into the flask, and the whole brought again to the boil.

Further additions of the solutions are run in, and after each addition the flask and contents are boiled up.

The blue colour of Pavy's solution will be seen to fade after each addition and boiling, and the estimation is finished when the blue colour has completely faded.

10 c.c. of Pavy's solution being equivalent to 5 mgrm. of glucose (by experiment), the reducing power of the solution to be determined in terms of glucose is readily calculated from the number of cubic centimetres of that solution required to decolourise 10 c.c. of Pavy's solution.

Total Nitrogen and Albuminoid or Proteid Matter.

In unadulterated plain cocoa and chocolate, the cacao matter is the only nitrogen-containing constituent. In milk chocolates, however, the presence of casein in the milk solids employed will increase the nitrogen and consequently the albuminoid values.

The use of ammonia in the production of "soluble" cocoa powder may also increase the amount of nitrogen found by the Kjeldahl method recommended.*

Total Nitrogen (Kjeldahl's Method modified by Gunning, Arnold, etc.).

1 grm. of the sample is introduced into a flask of hard Jena glass, and treated with 20 c.c. of strong sulphuric acid, a small globule of mercury being added at the same time.

The flask is loosely closed by a ball stopper, and gradually heated over a naked Bunsen flame.

After the frothing has ceased the heat is increased till the whole is briskly boiling, when 10 grm. of purest potassium bisulphate (absolutely free from any ammonium salts) are added.

The flask and contents are heated until the solution is quite clear and colourless, when they are cooled down and washed into a large distilling flask bearing a doubly perforated cork.

Through one hole of the cork is passed a thistle funnel provided with a stopcock, and through the other a tube connected to a condensing apparatus.

A sufficient quantity of a solution of sodium hydrate (containing a little sodium sulphide) is passed through the funnel to more than neutralise the acid solution in the flask, and some small pieces of zinc foil are added to prevent bumping when the contents of the flask are boiled.

The ammonia is distilled off and collected at the end of the condenser into a known volume of $\frac{N}{10}$ sulphuric acid, the loss of acidity of the standard acid being later estimated by titration with $\frac{N}{10}$ sodium carbonate or hydrate solution. The loss of acidity of the standard acid solution

* A. Stutzer, 'Zeitsch. angew. Chem.,' 1892, 510.

is due to the absorption of ammonia distilled from the alkaline solution in the flask, and when this value is known the equivalent of nitrogen in the ammonia found, and originally present in the sample, can be readily calculated.

The total nitrogen multiplied by 6·25 will give approximately the albuminoid matter.

If, however, it is required to estimate the amount of nitrogen from the vegetable albumen alone, it is necessary to prepare the sample before submitting it to the Kjeldahl process.

Estimation of Nitrogen from Albumen (Stutzer's Method).

From 1 to 2 grm. of the sample are finely divided and boiled for a few minutes with 100 c.c. of water. 0·4 grm. of moist copper hydrate are added, and, after cooling, the liquid is filtered through a filter-paper and the residue thoroughly washed with water. The filter-paper and contents are then submitted to the Kjeldahl process.

The difference between the total nitrogen and that found by Stutzer's method will give the non-albuminoid nitrogen, which in the case of pure cacao will result almost entirely from theobromine and caffeine.

In all cases of estimation of nitrogen by Kjeldahl's method, a blank experiment should be conducted side by side with the actual determination, in order to eliminate the errors caused by any impure and nitrogen-containing chemicals.

Starch.

The amount of starch present in pure cacao never exceeds 12 per cent., the usual quantity found being 9 per cent. The addition of foreign starch, which, as a cheap adulterant, may be found in the commonest chocolate and cocoa powders, and also in the majority of chocolate powders, will rapidly increase the starch figure.

Bordas has shown that the percentage of starch found in commercial cocoa is practically a constant, amounting to 9·34 per cent. on cacao mass and 28·5 per cent. calculated on cacao matter insoluble in water. On this assumption he calculates the approximate amount of cacao matter present in a preparation, and is able to estimate the amount of adulteration with foreign starch, if such has been detected under the microscope. The starch may be estimated by any of the recognised methods, by hydrolysis of the starch by diastase or mineral acids, and estimating the sugars formed.

Method I (Dubois Method for Cocoa Preparations in the Absence of Sugar).*

2 grm. of the sample are transferred to a 500 c.c. Erlenmeyer flask, to which are added 20 c.c. of water and 12 c.c. of strong sulphuric acid. The latter is cautiously added with a slow rotation of the flask. The mixture is heated over a low flame with constant rotation until the colour changes from brown to reddish-black. The time required for this change has been found to be approximately one and one fourth minutes, so that all samples should be treated for this time.

30 c.c. of water are then added, the mixture heated to boiling, and boiled for fifteen seconds. A little cold water is poured in, the flask quickly cooled, and the acid nearly neutralised with a saturated solution of caustic potash.

The solution is then again cooled and transferred to a 250 c.c. flask, completing the volume with cold water; 50 c.c. of the filtrate are used for the determination of copper-reducing substance as dextrose (100 mgrm. dextrose = 0·2538 grm. copper oxide = 0·2027 grm. of copper).†

* W. L. Dubois, 'U.S. Dept. of Agric.,' 1910, Bull. 132.

† Brown, Morris and Millar, 'Journ. Chem. Soc.' (Trans.), lxxi, 281.

Method II (For Cocoa Preparations containing Sugar and Soluble Carbohydrates).

4 grm. of the sample are shaken with petroleum ether until the whole of the fat has been removed.

After filtration and a further washing with ether, 100 c.c. of water are added to the contents of the flask, and the residue on the filter-paper is washed back into the flask. The flask is thoroughly shaken and the contents filtered through a filter-paper. After three or four washings with water, and after the whole of the sugar has been removed, the filtrate is made up to 500 c.c. and may be used for sugar estimation, whilst the residue is washed into an Erlenmeyer flask and treated as described in *Method I* for estimation of the starch.

Dubois, by employing these methods, obtained 10·77 per cent. to 13·05 per cent. of starch in cocoa nibs, 11·38 per cent. to 13·64 per cent. in bitter chocolate, and 7·4 per cent. to 8·5 per cent. in sweet chocolate. In later experiments the same author obtained 16·3 per cent. to 19·8 per cent. of starch in cocoas, and 10·4 per cent. to 18·2 per cent. in bitter chocolates.

Welmans* has estimated the quantity of commercial dextrin added to chocolate. The dextrin is detected by treating the cacao preparation, after extraction of fat, with water.

The solution is filtered, and to 10 c.c. of the filtrate 40 c.c. of 90 per cent. alcohol added, when, if dextrin is present, an immediate turbidity is produced. The dextrin may be quantitatively precipitated by lead acetate in the presence of ammonia.

Method III (approximate).

A method for determining the approximate amount of starch present in a cacao preparation has been devised by Dragendorff.

* P. Welmans, 'Zeitsch. öffent. Chem.,' v, 478.

2 to 3 grm. of the dry fat- and sugar-free (see *Method II*) material are heated with 25 to 30 c.c. of a 5 per cent. alcoholic potassium hydrate solution for 20 hours on a water bath. The hot solution is then filtered through a weighed ash-free filter-paper and the residue washed successively with hot alcohol, cold alcohol and hot, but not boiling, water. The filter and contents are then dried and weighed (1). The loss in weight corresponds to albuminoid matter, sugar and soluble salts. The filter-paper and contents are then cut into fine pieces with scissors and boiled with 5 per cent. hydrochloric acid solution until the solution no longer gives a blue reaction with iodine. The solution is then filtered through a weighed filter, and the residue washed, dried and weighed (2). The difference between the weights of Nos. (1) and (2) gives very closely the amount of starch present. This value may be checked by estimating the amount of dextrose present in the filtrate from No. (2).

Sugar (Sucrose or Cane Sugar, Lactose or Milk Sugar).

When solutions of cane sugar are boiled with mineral acids, the sugar is split up or inverted into two glucoses, the one rotating a plane of polarised light to the right and hence called dextrose, the other rotating to the left and called levulose. These two sugars are capable of reducing copper solutions, as already described.

Carbohydrates, among which cane sugar, milk sugar, etc., are numbered as being soluble in water, are usually estimated by a combination of physical and chemical processes. When the sugars are present individually their determination is not a matter of great difficulty, but when more than one sugar is present in a preparation, their isolation and determination may be one of considerable complication.

In the case of cacao mass, the reducing matters present have already been shown to be small, and the power

possessed by a cold water extract of cacao of rotating polarised light is negligible. If, therefore, as in the case of a plain chocolate or chocolate powder, the sugar present is cane sugar only, the direct estimation of the sugar becomes a simple process by testing the reducing power of an inverted cold water extract of a weighed sample, or by testing its power of rotating polarised light.

In this chapter the process of testing the reducing power of a cold water extract has been described under "Reducing Matters," though in order to render cane sugar capable of reducing a copper solution (either Fehling's or Pavy's) it is necessary to invert it.

Method I.

Inversion of Cane Sugar and Estimation by Reduction of Copper Solutions.

To the clarified aqueous solution containing the sugar from a weighed quantity of chocolate add a few cubic centimetres of strong hydrochloric acid, and heat to boiling for ten minutes. Then place the vessel containing the solution aside for about ten hours, and estimate the inverted sugar by Pavy's or Fehling's solution (*vide* "Estimation of Reducing Matters," *Methods I and II*).

If the copper solutions have been previously standardised against a solution of inverted pure cane sugar of known strength, the value of a given number of cubic centimetres of copper solution for complete precipitation or decolourisation in terms of cane sugar will be known.

Method II.

Estimation of Cane Sugar by Polarimetric Methods.

The power of rotating polarised light possessed by the sugars affords a ready means for their estimation.

The apparatus in which such estimations are made consists essentially of one stationary Nicol prism and a rotating

prism attached to a circular scale. According to the instrument used the scale is made to give readings as degrees or as direct percentage of cane sugar (saccharimeter). The first prism polarises the light, whilst the second determines the plane of the polarised light coming from the first.

The means of obtaining the readings are too well known to need description here.*

The estimation of a sugar in solution can be made (if only one sugar is present) by observing the angle of rotation of that solution in a tube of known length, when, if the specific rotatory power † of the particular sugar is known, the following equation will serve for determining the weight of sugar in 1 c.c. of the solution :

$P = \frac{a}{[a]\,l}$ where a = observed rotation of the solution,

$[a]$ = specific rotatory power of the particular sugar,

l = length of observation tube in decimetres.

As an example: The observed rotation of a cane sugar solution in a 1 decimetre tube is 5°, and the specific rotatory power of cane sugar being 66·5°, the percentage content of sugar in that solution

$$= \frac{5 \times 100}{66{\cdot}5 \times 1} = 7{\cdot}518.$$

The specific rotatory powers of individual sugars have been carefully estimated by a number of observers; thus, sucrose (cane sugar) = + 66·5°; maltose (malt sugar) = + 138·0°; lactose (milk sugar) anhydrous = + 55·4°; lactose crystalline = + 52·6°; dextrose = + 51·3°; levulose = − 95·4°; invert sugar = − 22·0°.

In saccharimeters or polarising apparatus especially

* For full particulars see Landolt, 'Optical Rotation of Organic Substances,' 1902, 325.

† The specific rotatory power of a sugar is the number of degrees of rotation observed when 1 grm. of the sugar is dissolved in 1 c.c. of fluid and observed by yellow light through a tube 1 decimetre long.

adapted for determining the quantity of cane sugar in solutions, the scale attached to the analysing prism is divided so as to read the percentage of cane sugar direct.

The official method for determining the percentage of cane sugar in chocolate according to the German decree of May 31st, 1891, is as follows: 13·024 grm. of chocolate are damped with alcohol, then warmed for fifteen minutes with 30 c.c. of water on a water bath. Whilst still hot, the solution is poured onto a wet filter-paper, and the residue again treated with hot water until the filtrate nearly equals 100 c.c. The filtrate is mixed with 5 c.c. of basic lead acetate solution, allowed to stand for fifteen minutes, clarified with alum to which a little alumina has been added, made up to a definite volume (110 c.c.) and polarised.

In plain chocolates and chocolate powders it is improbable that any other sugar than cane sugar will be found. In special preparations, maltose, lactose, etc., will occur, due to the addition of malt powders, milk solids, etc., and consequently variations in the methods of estimation will be necessary.

As milk chocolates have now become so popular, it is intended to give methods by which lactose can be determined in the presence of cane sugar. The following method, which has been devised by Dubois,* is recommended by the A.O.A.C.:

Method III.

Examination of Lactose and Sucrose in Milk Chocolate Preparations (Dubois' Method).

13 grm. of the sample are freed from fat by shaking and centrifuging with two separate quantities of gasoline (100 c.c.).

The solvent is separated by decantation and the residue treated with 100 c.c. of water, and shaken for ten minutes.

* W. L. Dubois, 'U.S. Dept. of Agric.,' 1907, Bull. 107.

5 c.c. of basic lead acetate solution (for preparation see p. 307) are added, the precipitate filtered off, and the excess of lead removed from the filtrate (original filtrate).

25 c.c. of this solution are allowed to stand overnight to destroy bi-rotation, and then polarised. Multiply the readings so obtained by 2 (Result A).

Invert (for method of inversion see p. 307) 50 c.c. of the original filtrate, and nearly neutralise the acid, after cooling, with sodium hydrate solution. Make up the combined solution to 100 c.c. with water, and bring to the temperature at which the direct readings were taken and polarise. Multiply the readings by 4 (Result B). Using the same solution, polarise again at 86° C. in a water-jacketed tube, and multiply the readings by 4 (Result C).

The approximate weights of sucrose and lactose present in the 13 grm. of sample are obtained by the following formulæ:

$$\text{Grammes of sucrose} = \frac{(A-B) \times 1{\cdot}05 \times 13}{142{\cdot}66 - \frac{t}{2}}$$

$$\text{Grammes of lactose} = \frac{C \times 1{\cdot}264 \times 1{\cdot}11 \times 1{\cdot}05 \times 13}{100}$$

$$= \frac{19{\cdot}152\ C.}{100}$$

In these formulæ the factors are explained as follows:*

1·05 is the factor to allow for the increase in volume of the solution occurring on addition of 5 c.c. of lead acetate solution.

1·264 is the factor allowing for the difference in normal weight of sucrose and lactose, thus $\frac{32{\cdot}884}{26{\cdot}00} = 1{\cdot}264$.

1·11 is the factor for reducing readings taken at 86° C. to readings taken at 20° C.

A = Direct readings of normal weight of material.

* W. L. Dubois, 'Journ. Amer. Chem. Soc.,' 1907, xxix, 556.

B = Invert readings of normal weight of material.
C = Invert ,, ,, ,, at 86° C.

From the total amount of sugar found by this method the percentage of sugars present is calculated by the following formulæ:

$$\frac{(A-B)\ 1\cdot05\ X}{142\cdot66 - \frac{t}{2}} = \text{Percentage of sucrose.}$$

$$(1\cdot473)\ X = \text{Percentage of lactose.}$$

This correction is necessary from the experiments of Dubois, conducted at 20° C., to the following extent:

For 2 grm. of sugar in sample	. .	X = 101·20
,, 4 grm. ,, ,,	. .	X = 102·50
,, 6 grm. ,, ,,	. .	X = 103·60
,, 8 grm. ,, ,,	. .	X = 104·80
,, 10 grm. ,, ,,	. .	X = 106·05
,, 15 grm. ,, ,,	. .	X = 109·40
,, 20 grm. ,, ,,	. .	X = 112·40

Official Method of Inversion.

To 5 c.c. of the clarified solution free from lead, add 5 c.c. of 38·8 per cent. hydrochloric acid solution, and set aside for twenty-four hours at a temperature not below 20° C., or if the temperature be above 25° C., for ten hours.

Preparation of Lead Acetate Solution.

Boil 430 grm. of normal lead acetate, 13 grm. of lead oxide (PbO) with 1000 c.c. of water for half an hour. Cool the mixture and allow to settle. Decant the clear solution, and dilute with recently boiled water till the specific gravity = 1·25.

For further information regarding the estimation of sugars by polarimetric methods Landolt's book on 'The Optical Rotation of Organic Substances' is to be recommended.

Estimation of Milk Solids in Milk Chocolate.

Estimations of nitrogen and nitrogenous matters, the chemical and physical constants of the fat and the estimation of the lactose present afford means by which the amount of total milk solids in the chocolate can be calculated. Seeing that milk solids from full cream contain 25 per cent. of fat, 38·5 per cent. of lactose, and about 27·5 per cent. of nitrogenous matters, whilst cacao mass contains about 50 per cent. of fat (with different chemical and physical constants to butter fat), practically no reducing matters, and about 15·5 per cent. of nitrogen-containing bodies, the proportions of added milk solids can be readily estimated. By careful consideration of the chemical and physical constants of the fat it can be determined whether the milk solids were obtained from full-cream milk, the Reichert-Meissl value being especially useful in determining the proportions of the fats present.

Cacao Matter.

The amount of cacao matter present in chocolate, etc., assumes a certain importance, seeing that a rebate is to be allowed on exported cacao matter which has previously paid duty on entering this country.

The direct estimation of cacao matter is obviously an impossibility, as cocoa is composed of a number of complex chemical constituents, and the amount of cacao matter actually present can only be obtained by indirect means.

Undoubtedly the most satisfactory method is complete analysis of the preparation, when, after it has been found that no foreign starch, mineral matter, husk, etc., have been added, the difference between 100 and the percentages of sugar (if any) and total fat will give a very close value for the amount of fat-free cacao matter present.

Booth, however, obtains the proportion of fat-free cacao matter on the assumption that the cold water extract is for all practical purposes identical in husk and nib. The cold water extract is assumed to be 12 per cent. of the total cacao, and after the sample under investigation has been corrected for (*a*) the sugar, as ascertained by the polarimeter, and (*b*) for the extract of any cereal that may be present (7·7 per cent. for wheat, 5·1 per cent. for barley, 0·8 per cent. for maize or cornflour, 0·9 per cent. for rice, 1·98 per cent. for sago, and 0·4 per cent. for arrowroot), the residual figures multiplied by $\frac{100}{24}$ will give the dry fat-free cacao matter present.

If this agrees with that obtained by multiplying the corrected nitrogen by 20 (the factor for fat-free nib) then no shell is present. If it does not agree, then the following formula is recommended for calculating the respective proportions:

$$y = 40\,N - x$$

where x = the percentage of fat-free cacao matter found as above,

y = the percentage of fat-free nib,

N = total nitrogen due to cacao matter.

In a husk-free cocoa containing 12 per cent. of cold water extract, 50 per cent. of fat and 2·5 per cent. of nitrogen, the two equations will be found to agree thus:

$$\text{Dry fat-free cacao matter} = \frac{12 \times 100}{24} = 50 \quad (1)$$

$$y = 100 - 50 = 50 \quad . \quad . \quad . \quad (2)$$

Bordas has made use of somewhat similar means for the estimation of the amount of cacao matter in a preparation; thus in a pure cocoa powder or preparation free from sugar, starch, etc., the following equations should hold good:

1·30 × (cacao matter insoluble in water) = (dry fat-free

cacao matter), and 2·95 × (cacao matter insoluble in water) = (dry cacao matter).

The factor 32·85, which is the value for (cacao matter insoluble in water), found to be practically constant for eleven different varieties of cacao, is applicable also to cocoas which have been rendered soluble by treatment with alkali.

In the estimation of cacao matter in a preparation, Bensemann's figures, which are tabulated, showing the relations between starch (S), fat (F), and the insoluble matter of cacao (U), may be found useful.

TABLE LV.—*Numerical Relations between the Various Constituents of Cacao.*

	$\frac{S}{U-F}$	$\frac{F}{U-S}$	$\frac{S}{U}$	$\frac{F}{U}$	$\frac{S}{F}$
Air-dried husked beans:					
Maracaibo	0·4289	0·7395	0·1636	0·6185	0·2645
Caracas	0·4074	0·7273	0·1578	0·6125	0·2577
Trinidad	0·3452	0·7297	0·1247	0·6387	0·1953
Guayaquil Machala	0·3583	0·7330	0·1297	0·6379	0·2033
Porto Plata	0·3660	0·7734	0·1481	0·6589	0·2247
Means	0·3946	0·7406	0·1446	0·6335	0 2283
Air-dried husks:					
Maracaibo	0·1390	0 0412	0·1341	0·0357	3·7564
Caracas	0·1525	0·0356	0·1479	0·0304	4·8674
Trinidad	0·1515	0·0467	0·1455	0·0399	3·6413
Guayaquil Machala	0·1272	0·0402	0·1227	0·0352	3·4827
Porto Plata	0·1850	0·0797	0·1728	0·0660	2·6202
Means	0·1508	0·0484	0·1446	0·0414	3·4920
Chocolate in cakes mixed with sugar only:					
4·8 marks per lb.	0·3838	0·7303	0·1438	0·6253	0·2300
4·0 „ „ „	0·3476	0·7161	0·1314	0·6220	0·2112
3·2 „ „ „	0·3310	0·7226	0·1207	0·6354	0·1899
2·4 „ „ „	0·3029	0·7035	0 1141	0·6232	0·1831
2·0 „ „ „	0·3729	0·7490	0·1298	0·6517	0·1992
Means	0·3480	0·7245	0·1282	0·6317	0·2029

APPENDIX

PROVISIONAL DEFINITIONS AND STANDARDS OF CACAO AND ITS PREPARATIONS.*

(1) Pure Cacao Mass, Paste, or Bitter Chocolate.

To consist of the crushed nibs of roasted and husked cacao beans only; it must not have been treated with alkalis or partially defatted.

To contain not less than 45 per cent. cacao butter.

,, more than 4 per cent. ash or mineral matter. (Ratio of soluble to insoluble ash to not exceed 2 : 3.)

,, ,, 6 per cent. moisture.

,, ,, 2·75 per cent. pentosans.

,, ,, 13 per cent. starch (which must be ascertained to be due to the cacao only, by means of the microscope).

To be free from added or included husk, cacao butter substitutes, starch, sugar, flavouring matter, etc.

(2) Pure Cocoa Powder.†

To consist of partially defatted pure cacao mass only.

To contain not more than 6 per cent. of moisture.

,, ,, 5 per cent. of ash or mineral

* The provisional standards given herein are essentially the same as those proposed by the author at the Congress of Cocoa and Chocolate Makers held at Berne in August, 1911.

† All cocoa and chocolate preparations (exclusive of cacao mass, paste or bitter chocolate and cacao butter) may contain small quantities of harmless flavouring matters, which shall not include alkalis and other mineral chemicals.

matter (to show an alkalinity not exceeding 3 per cent as K_2O on the dry, fat-free cacao matter).

To contain not more than 3·5 per cent. pentosans.

„ „ 16 per cent. starch (which must be ascertained to be due to the cacao only, by means of the microscope).

To be free from added or included husk, alkali, starch, sugar, etc.

(3) Soluble Cocoa Powder.*

To consist of pure cocoa powder (as above) treated with alkali.

To conform with the standards of pure cocoa powder, with the exception that the ash limit may be increased to 7 per cent., though the alkalinity may not exceed 5 per cent. estimated as K_2O on the dry fat-free cacao matter.

(4) Pure Cacao or Cocoa Butter.

To consist of the expressed fat of pure cacao mass only, or if extracted from the husk to be so declared.

To conform with the British Pharmacopœia standard of purity, and to give chemical and physical constants falling within the following limits:

Zeiss butyro-refractometer value at 40°C.	46°–47°.
Saponification value	192°–195°.
Iodine value	34°–42°.
Reichert-Meissl value	0·2°–0·9°.

To be free from all animal and foreign vegetable oils and fats.

(5) Chocolate Powders.*

The word "pure" to be applied only to those chocolate

* For reference, see p. 311 (second foot-note).

powders which contain pure cacao mass and fine crystallised sugar without further additions.

A removal of a portion of the fat from the cacao mass should not be allowed.

Pure Chocolate Powders.

To contain not more than 70 per cent. of sugar.

,, less than 30 per cent. pure cacao mass (estimated to contain 50 per cent. cacao butter).

The proportions of moisture, ash, starch, pentosans, etc., will be in accordance with the amount of cacao matter used.

If starch is added, the powder must not be labelled "pure," and the nature and quantity of the starch added should be clearly stated on the label, wrapper, etc. The extent of defatting of the cacao mass (if such has been made) should also be stated.

(6) Sweetened Chocolate.*

The term "chocolate" (with or without the word "sweetened") to be applied only to those preparations which consist of pure cacao mass, fine crystallised sugar, and additional cacao butter (if desired) only.

To contain not more than 65 per cent. of sugar.

,, less than 32 per cent. of pure cacao mass (estimated to contain 50 per cent. cacao butter).

The proportions of moisture, ash, starch, pentosans, etc., will be in accordance with the amount of cacao matter used.

(7) Milk Chocolate.*

To consist of pure cacao mass, finely divided sugar and the solids of milk only.

* For reference, see p. 311 (second foot-note).

The solids of the milk should be obtained from full-cream milk, and should be free from antiseptics.

To contain not less than 15 per cent. of milk solids.			
i. e.	,,	,,	3·75 per cent. of milk fat.
	,,	,,	5·50 per cent. of milk sugar.
	,,	,,	3·75 per cent. of proteids (over and above that due to the cacao matter present).

If no other fats than cacao butter and milk fat are present, the fat extracted from a milk chocolate containing 25 per cent. milk solids, 10 per cent. cacao mass (containing 50 per cent. cacao butter), 15 per cent. added cacao butter, 50 per cent. cane sugar, will show the following chemical and physical constants :

Zeiss butyro-refractometer value at 40° C. .	45·5
Saponification value	199·4
Iodine value	35·6
Reichert-Meissl value	9·23

(8) Covering Chocolate.*

To consist of variable quantities of pure cacao mass, finely crystallised sugar and additional cacao butter only.

(9) Nut, Malt, and other Fancy Chocolates.*

To consist of variable quantities of pure cacao mass, sugar, nuts, malt, etc., and to bear a label indicating the nature of such additions.

(10) Chocolate Bon-bons.*

To consist of "fondants," "fruit jellies," etc., covered with pure covering chocolate.

* For reference, see p. 311 (second foot-note).

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